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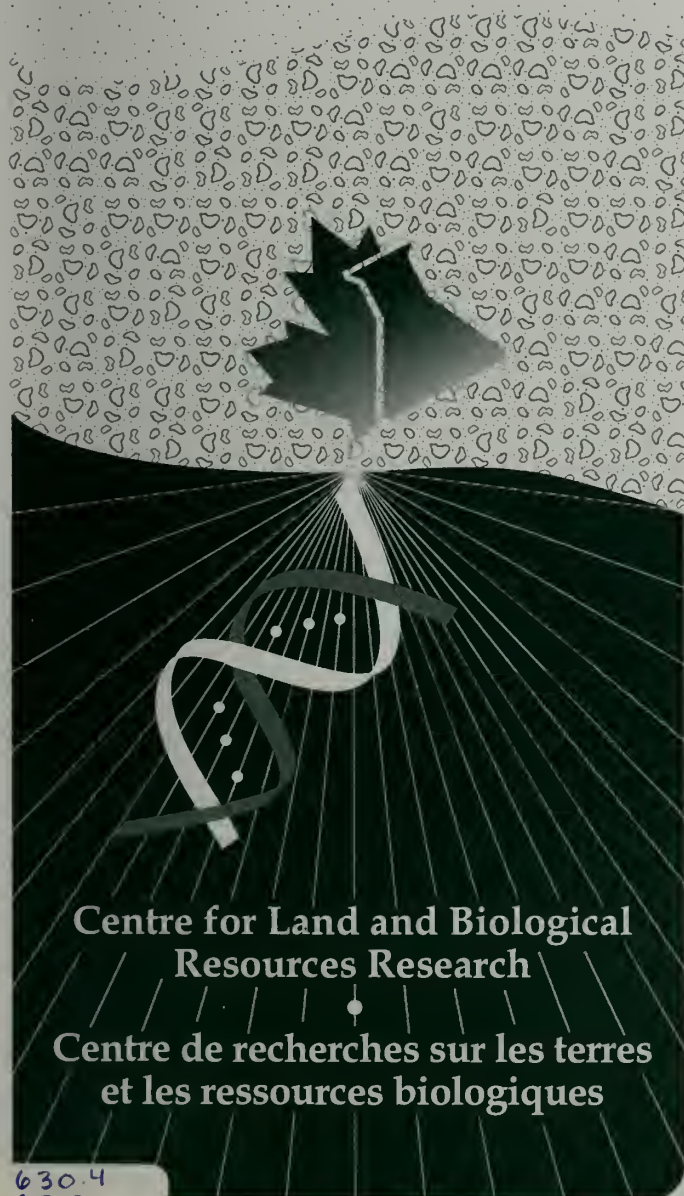
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# Concentrations and variability of major, minor and trace elements in soils and crops from two Humic gleysol fields in Southeastern Ontario, Canada.



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# **Concentrations and variability of major, minor and trace elements in soils and crops from two Humic gleysol fields in Southeastern Ontario, Canada.**

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## PREFACE

Concentrations, chemical forms and mobility of trace elements in soils and their availability to the food chain are the basis for the nutritional and toxicological status of crops, animals and human consumers of foods therefrom. Over one dozen trace elemental constituents of rocks and soils are essential at low levels for plant and/or animal nutrition. At higher concentrations many of these essential trace elements together with other toxic elements may affect the safety and quality of food. Agricultural production can also be affected by both excesses and deficiencies of trace elements. Current environmental concerns over pollution caused by and impacting on agricultural practices are focusing on contamination of our soil resource by toxic elements and their uptake by food and feed crops, but there is a lack of reliable information regarding the levels of nutritionally and environmentally important elements in soils and crops. Multielement analyses of soils and crops are thus essential for correlations and interpretation and for uncovering hitherto unknown elemental relations.

This technical bulletin is a detailed account of an investigation primarily into the minor and trace but also major element status of an agricultural soil and two crops grown thereon from farmland in Southeastern Ontario. Information herein provides a reliable database regarding background levels of a large number of minor and trace elements in an important agricultural soil as well as for establishment of soil-crop-element correlation relationships and influences of long term agricultural practices. It can serve as an information base and a methodological guide to researchers in soil and environmental sciences.





## SUMMARY

Surface (Ap) and subsoil (Bg) horizons of an Orthic Humic Gleysol soil (Haplaquoll-US description) from two cultivated fields in Southeastern Ontario together with corn (Zea mays L.) and alfalfa (Medicago sativa L.) crops were analyzed for a range of macro, minor and trace elements of nutritional, toxicological and environmental significance to establish background levels and spatial variability. Reliable total concentrations were established for 10 samples of each commodity from one transect per field for the minor and trace elements, Ba, Be, Co, Cr, Cu, La, Mn, Ni, P, Sr, V, Yb and Zn in soils, Al, Ba, Cu, Fe, Mn, Na, Si, Sr, Ti and Zn in corn leaves, corn stalk and alfalfa, as well as the major elements Al, C, Ca, Fe, K, Mg, Na, Si and Ti in soils and Ca, K, Mg, P and S in crops.

Within one or the other field, significantly different variations in concentration were observed among the 10 m sampling locations in the Ap horizon for Al, Ba, C, Cr, Cu, La, P, Si and Yb and in the Bg horizon for Cr, Fe, La, Mg, Mn, Na, Ni, P, Si, Sr, Yb and Zn. All elements with the exception of Ba, in both fields, Ca and Na in the corn field, and P in the alfalfa field, exhibited statistically significant concentration differences between the two horizons. Mean concentrations of Al, Be, Ca, Cr, Fe, La, Mg, Na, Ni, P, Si, Sr, Ti, V and Zn in the Ap horizon differed significantly between the two fields whereas in the Bg horizon only Ba, Mn, P and Zn were different.

Elemental concentrations were generally highest in the clay fractions followed by levels in silt and sand with the exception of Ca, K, Mn, Na, Si and Sr which exhibited the reverse or no trend. Levels for most elements were lower in fractions derived from the surface horizon. Highly significant differences were exhibited between the two fields for K and Sr in sand, Ba, Cu, Ni and Zn in silt, and Ba and Be in clay.

Concentrations of all elements with the sole exception of K were either equal in the two corn tissues or were higher in the leaves. Most elemental concentrations differed significantly between corn tissues and alfalfa with Ca much higher and K lower in alfalfa than in corn tissues.

Determinations were also made of DTPA-, EDTA- and HCl- extractable Cd, Co, Cr, Cu, Mn, Ni, Pb, V and Zn in soils and correlations were established among extractable and total levels. Silt and clay fractions were characterized for 11 minerals and phases: interstratified mineral, smectite, vermiculite, chlorite, mica, kaolinite, amphiboles, quartz, microcline, plagioclase and X-ray amorphous material with generally similar contents observed in both fields.

This information provides a database regarding background levels of minor elements in an important agricultural soil as well as for establishment of soil-crop-element correlation relationships and influences of long term agricultural practices.



## INTRODUCTION

The concentrations, chemical forms and mobility of trace elements in soils and their availability to the food chain are the basis for the nutritional and toxicological status of crops, animals and human consumers of foods therefrom. In addition to the requisite macro elements, over one dozen trace elemental constituents of rocks and soils are essential for plant and/or animal nutrition; these include B, Co, Cu, F, Fe, I, Mn, Mo, Ni, Se, Si, Sn, V and Zn. At elevated concentrations many of these essential trace elements together with others such as As, Be, Cd, Cr, Hg and Pb, may be toxic to crops and/or animals or may affect the quality of foods for man. Agricultural production is affected by both excesses and deficiencies of trace elements as these occurrences lead to nutritional or toxicological problems in plants and animals resulting in crop failure and animal losses (Horvath, 1972; Shamberger, 1979; Kubota 1980; Thornton, 1981; Webber, 1981). Current environmental concerns over pollution caused by and impacting on agricultural practices are focusing on contamination of our soil resource by toxic elements and their uptake by food and feed crops (Wolnik et al 1983a, 1983b, 1985; Shacklette 1980; Webber and Shames, 1987).

Manifestations of toxic trace elements do not occur in isolation and a number of synergistic and antagonistic interactions have been established at both deficiency and excess concentrations (Underwood, 1979). These interactions involve major elements as well as trace elements and for this reason knowledge of concentration levels of elements other than those being specifically studied or monitored is vital. Multielement analyses of soils and crops are thus essential for correlations and interpretation and for uncovering hitherto unknown elemental relations. The Multielement approach followed by Ure and coworkers (1979) in characterizing Scottish soils for some 60 elements is commendable.

The status of the trace element discipline is covered in reviews dealing with soils (Vinogradov, 1959; Aubert and Pinta, 1977), plant food and feedstuffs (Shacklette et al, 1978), and both soils and crops (Horvath, 1972; Webber, 1981; Mortvedt et al, 1972; Sillanpää, 1982; Kabata-Pendias and Pendias, 1984). With respect to Canadian soils, McKeague and coworkers (McKeague et al, 1979; McKeague and Wolynetz, 1980) have summarized existing information on background levels of minor elements and have contributed additional experimental results. More specific to the Southeastern Ontario soils of interest in this work are the publications (Frank et al, 1976; Whitby et al, 1978) presenting minor and trace element levels in Ontario soils. The basis for establishing elemental relevances and interrelationships in soils and crops is the sufficiently reliable and valid analytical database stemming from the proper and careful application of analytical approaches throughout the investigation (Shacklette et al, 1978; Ihnat, 1983).

The objectives of this research investigation were (a) to obtain background concentration levels of minor elements in a selected important Canadian agricultural soil in Southeastern Ontario, (b) to determine the spatial variability of these concentrations in cultivated surface and subsoil horizons, (c) to establish correlations among the elements, soils and crops grown thereon and (d) to get an estimate of possible influences of long term agricultural practices on the distribution of minor elements in surface and subsoils. Reported herein are experimental and analytical details, total background



elemental concentration levels for a suite of minor trace as well as macro elements in soil horizons, sand, silt and clay fractions and crops, extractable concentrations of a number of trace elements in the soils, spatial variability of soil elemental levels within and between fields and horizons, statistical correlations among the elements, soils, fractions and crops grown thereon, and estimates of possible influences of long term agricultural practices on the concentration and distribution of minor elements in soils.

## EXPERIMENTAL

### Sampling of Soils and Crops

The sites selected were two adjacent farm fields in Nepean on the outskirts of Ottawa at the SW (field 1) and NW (field 2) corners of the intersection of Fallowfield and Merivale roads, corresponding to sites 1A and 1C, respectively in the previous study by Wang et al. (1985). The dominant clayey marine soil of both fields is classified as a Brandon series, an Orthic Humic Gleysol by the Canada Soil Survey Committee (1978) and an Haplaquoll according to the Soil Taxonomy (Soil Survey Staff, 1975), with clay to clay loam surface horizon (Ap), clay to silty clay subsoil (Bg) and angular blocky structured parent material. Both sites are tile drained with field 1 seeded to continuous corn (*Zea mays* L.) for 12 years, and field 2 seeded for at least 12 years with alfalfa hay (*Medicago sativa* L.). Field 1 was fertilized annually with ca 120-30-70 kg of N-P-K per ha; field 2 had much less chemical fertilizer but more animal manure added. The corn field was fall-ploughed and disked in the spring.

For collection of soil and crop samples, a random transect (Wang, 1982) was run along each field and samples were taken in August 1982 at ten 10 metre intervals along each transect. At each sampling location, duplicate ca 200 g samples of the 0-15 cm plow layer (Ap horizon), and 50-60 cm subsoil (Bg horizon) were taken and placed in separate 180 ml polyethylene or polypropylene bottles. A total of 20 Ap and 20 Bg samples were taken from the two fields. Also at each sampling location either one entire corn plant or a grab sample of alfalfa closest to the soil collection site was cut near ground level and placed in a polyethylene bag. Typical heights were about 1.2 m and 0.3 m for the corn and alfalfa crops, respectively, with alfalfa being the second growth that season after a first cut one month earlier. No alfalfa was growing in the vicinity of location 4 in field 2. Samples were transported to the laboratory and processing was begun immediately that afternoon and evening.

### Sample Processing

Soil samples were air-dried, then gently crushed and sieved through nylon sieves to prepare <2 mm material according to a standard method (McKeague, 1978). Further processing, analytical work and all data reported is on the basis of this soil material. Soil fractions of sand, silt and clay were prepared following pretreatment with  $H_2O_2$  to remove organic matter (McKeague, 1978). For total elemental analyses requiring total dissolution of soil materials, whole soils and sand fractions were finely ground in a motorized, porcelain mortar and pestle. Ten grams of well-mixed, air-dried, <2 mm sample was pulverized and sieved

through a 100 mesh nylon cloth. Material not passing through was returned to the mortar for further grinding and resieving, with the procedure repeated once more (for a total of three passes) to ensure greater than 99% recovery of starting material. Silt and clay fractions, being sufficiently fine, were not ground.

Fresh corn plants were separated into components, stalk, leaves, tassels, silk, corn and ear leaves. Component weights were determined for each sampling location, stalks and leaves were rinsed with distilled water, to remove soil splash, cut into small pieces and air-dried at ambient temperature. Alfalfa plants were used in their entirety; stems near roots were snipped off, remaining plant weighed, rinsed with distilled water and let air-dry. Corn stalks, leaves and alfalfa plants were ground to fine powders for chemical analysis, using a makeshift teflon<sup>r</sup> ball mill consisting of teflon<sup>r</sup> balls in a teflon vessel vibrating on a paint shaker, to minimize metallic contamination.

Whole soil (<2 mm) samples, ground whole soil, sand, silt and clay fractions and ground crop samples were subdivided and replicated as required for submission to laboratories conducting chemical, physical and mineralogical analyses.

#### Chemical Analysis - Soil Characterization

Characterization of soils for pH, total carbon, particle size distribution and exchangeable Ca, Mg and K was by usual methods (McKeague, 1978; Sheldrick, 1984). Determination of pH was in 0.01 M CaCl<sub>2</sub> using a 1:2 soil:solution ratio. Total carbon was determined by furnace combustion of 10 mg subsamples from 2 g of finely ground samples. Determinations of particle size including sand, silt and clay content were carried out by the pipette method following appropriate pretreatments. Exchangeable Ca, Mg and K were determined by flame atomic absorption spectrometry of filtrates following extraction with 2N NaCl.

For the determination of mineral composition, silt and clay fractions were examined by X-ray powder diffraction on oriented Mg-saturated samples before and after glycerol solvation, and after heat treatment at 550°C. The oriented samples were prepared by drying 30 mg of each sample suspended in 1 mL of H<sub>2</sub>O on a 25 mm x 30 mm glass slide. Glycerolation was achieved by using 1 mL of 2% glycerol - water solution instead of H<sub>2</sub>O in the procedure mentioned above. Analyses were carried out on an automated Scintag Pad V X-ray diffractometer with a graphite monochromator using Co-radiation. Mineral components were semiquantitatively determined by a method similar to that described by Kodama et al (1977).

#### Chemical Analysis - Soil and Crop Total Elemental Concentrations

Soil, soil fractions, and crop samples with blind replicates together with blindly-coded soil and plant reference materials were submitted to laboratories within the initiating establishment, CLBRR, and to laboratories of the Geological Survey of Canada, GSC, for total elemental chemical analyses. Both agencies carried out analyses on soil and crop materials for a range of elements within their respective repertoires complementing each other's work and purposely determining several elements in common.



In the CLBRR procedure for soils (based on procedures in McKeague, 1978; Ihnat, 1978; Ihnat, 1982; Pratt, 1965), 1 g of minus 100 mesh soil, sand, silt or clay was introduced into a 100 ml polytetrafluor-ethylene (PTFE, Teflon<sup>R</sup>) beaker, and wetted with a few drops of water. Concentrated HNO<sub>3</sub> (10 ml) was added, the beaker was covered with a PTFE cover and contents were refluxed for 0.5 h. Concentrated 70% HClO<sub>4</sub> (10 ml) was added, refluxing was continued for another 0.5 h, and the volume was reduced to ca 10 ml. Refluxing with an additional 10 ml of HClO<sub>4</sub> was repeated if the residue was not white, after which 10 ml 48% HF was added, refluxing was continued at a lower temperature for 0.5 h and the volume reduced to ca 5 ml. HF treatment was repeated and a check was made for complete dissolution. Following reduction to moist dryness (ca 2 ml) the solid residue was dissolved in 25 ml 2N HCl, and the solution was transferred to a 100 ml volumetric flask containing 10 ml of 10000 µg Cs/ml as CsCl to function as an ionization suppressor in flame atomic absorption measurements (FAAS). Minor and trace elements Co, Cu, Mn, Ni, Sr and Zn were determined by FAAS on a Varian AA6 atomic absorption spectrometer following established procedures (Ihnat 1981, 1982). Calibration was with mixed pure element standards using a quadratic version of the calibration curve.

Analyses of soils and fractions at GSC were by inductively-coupled plasma atomic emission spectrometry. Separate procedures were applied to the determination of the major elements, Al, Ca, Fe, K, Mg, Mn, Na, P, Si and Ti and the minor ones, Ba, Be, Co, Cr, Cu, La, Ni, Sr, V, Yb and Zn. For the major elements, 0.5 g of sample, previously heated 0.5 h at 900°C to oxidize S in order to obviate its detrimental effect on the analytical procedure, was fused with LiBO<sub>2</sub> in a graphite crucible, dissolved in 5% HNO<sub>3</sub> and made to 250 ml. Determination of elemental concentrations was with a Jobin-Yvon JY48 simultaneous emission spectrometer using solutions of standard rocks for calibration. For the minor elements, 1 g of material, again previously heated 0.5 h at 900°C, was treated with HNO<sub>3</sub> + HF + HClO<sub>4</sub>, taken to dryness and taken up in 10% HCl. The solution was filtered, filter paper with contents were fused with LiBO<sub>2</sub> in a platinum crucible, dissolved in HCl and pooled with the above filtrate to yield 100 ml of a final solution in 10% HCl. Determination was with the same instrument against mixed pure elemental standards for calibration.

Crop samples were analyzed in CLBRR laboratories by digesting 1 g with HNO<sub>3</sub> + HClO<sub>4</sub> and determining Ca, Cu, Fe, K, Mg, Mn, Na, Sr and Zn by FAAS with a Varian AA975 spectrometer against a mixture of pure elemental standards. In the GSC procedure, treatment was first with HNO<sub>3</sub> followed by a small quantity of HClO<sub>4</sub>. After being taken to dryness, the residue was taken up in 10% HCl and Al, Ba, Ca, Cr, Cu, Fe, Mg, Mn, Na, Ni, P, S, Sr, Ti, V and Zn were determined by emission spectrometry using the JY 48 spectrometer and pure element standard solutions. Si was measured by filtration and gravimetry.

#### Chemical Analysis - Soil Extractable Elemental Concentrations

Soil samples were analyzed in CLBRR laboratories for extractable trace elements using three different extractive procedures incorporating separately, DTPA, EDTA and HCl (Fiskell, 1965; Viets Jr. and Boawn, 1965; Lindsay and Norvell, 1978; McKeague, 1978; Sheldrick, 1984). The diethylene-triaminepentaacetic acid (DTPA) extracting solution contained 0.005M DTPA, 0.01M calcium chloride (CaCl<sub>2</sub>), and 0.1M triethanolamine [TEA, HOCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N] adjusted

to pH 7.30 with HCl. The ethylenediamine-tetraacetic acid (EDTA) solution contained 0.05M EDTA, 0.01M  $\text{CaCl}_2$  and 0.1M TEA while the third extractant was 0.1N HCl. Coarse soil (< 2mm) samples were extracted for 2 h, 0.5 h and 1 h using soil: extractant ratios of 1:2, 1:2 and 1:10 for the DTPA, EDTA and HCl extractions, respectively. Solutions were clarified by filtration through filter paper and Cd, Co, Cr, Cu, Mn, Ni, Pb, V and Zn were determined by FAAS.

#### Data Quality Control

Approximately 10% of soil and crop samples submitted to participating laboratories consisted of blindly-coded duplicates and reference materials to arrive at estimates of precision and systematic error. To monitor performance of soil analyses, for total elemental concentrations, aliquots of the CANMET soil reference materials SO-1, SO-2, SO-3 and SO-4 (Canadian Certified Reference Materials Project, CANMET, Energy Mines and Resources Canada, Ottawa, Ontario) were used, whereas for crop analyses, standard reference materials Citrus Leaves SRM1572 and Pine Needles SRM1575 from the National Institute of Standards and Technology (Office of Standard Reference Materials, Gaithersburg MD) were submitted. Precision of all elemental determinations was monitored via the duplicates. Estimates of analytical method reliability were possible for the following elements for which certified or recommended total elemental concentration values are available: soils - Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Si, Sr, Ti, V and Zn; crops - Al, Ba, Ca, Cr, Cu, Fe, Mg, Mn, Na, Ni, P, S, Sr and Zn. As no reference soil materials are available with certified values for extractable elements, control over the reliability of extractable concentrations was not possible.

## RESULTS AND DISCUSSION

#### The Database

For any meaningful interpretation and application of a numerical database the results therein must be of acceptable reliability for the task. Not only must the results be internally self-consistent ie. with good precision, but they must also be sufficiently accurate, ie. close to the truth, in order for correct manipulation and comparison with published work and that to appear in the future. This is especially so for the case of long term monitoring of soil properties where comparisons are made over space (different laboratories, locations) and time. Concerns of data quality including that in soil science have been raised (Shacklette et al 1978; Ihnat 1988, Cronce and Ciolkosz 1985; Driessen 1986) and effort has been made in this study to create a reliable elemental soil-crop database for use in this and subsequent publications. The approach taken was to involve several laboratories with complementary and overlapping analytical capabilities to generate reliable data. The premise is that concordance of analytical results on the same sample from different laboratories using different methods of analysis is a good indication of the reliability of these results. Furthermore, in addition to normal internal quality control measures taken within each laboratory, precision and accuracy were monitored by the incorporation of blind replicates and reference materials as available.



Analytical precision of total and extractable elemental concentration measurements was ascertained by incorporating blind duplicates of soil, soil fraction and crop samples at a rate of about 10%, into the sets of materials submitted for analysis to cooperating laboratories. Analytical precision (standard deviations) were computed for each element, laboratory and the different materials, soil and soil fractions (classed as one), corn leaves, corn stem and alfalfa. Homogeneity of variances was verified for the different crop tissues and levels using F tests, and variances were pooled as warranted. Further pooling of variances for all materials over laboratories was based on data selection to be mentioned below, to yield overall precision standard deviations recorded in Tables 1 and 2 for total and extractable elemental concentrations, respectively. These analytical precisions for the different elements, based on either one or both laboratories apply to the consolidated data (individual points) as plotted in Figures 2-8. With the exception of precision for total carbon, no specific measures of standard deviation were available for soil characterization properties plotted in Figure 1 save for general estimates for the particular method/laboratory available in the methods manual. Performance was, however, stated to be within limits published therein.

In Tables 1 and 2, analytical precisions for soil measurements are also presented as coefficients of variation,  $CV_A$ , estimated from precision standard deviations and mean elemental concentrations in the typically 40 samples from two horizons from the two fields. Estimates of mean overall coefficients of variation,  $CV_O$ , representing the scatter of data among sampling locations, as well as the ratios  $CV_A/CV_O$  are also included in the tables. This ratio ranges from 0.10 to 1.42, typically ca 0.4, for total element concentrations and from 0.11 to 1.50, typically ca 0.3 for extractable values, indicating the relatively small contribution analytical variation in this work makes to overall variability.

One aspect of this work which differs markedly from many other published soil studies, is the monitoring of data accuracy (total concentrations only) for soil and crop determinations using reference materials. The premise behind this is that good performance with an appropriate reference material run concurrently under identical operating conditions as the samples, is a reasonable indication of good performance also with the actual samples. Consequently, accuracy was monitored and estimated by the incorporation of soil and crop reference materials, soils CANMET SO-1, SO-2, SO-3 and SO-4 and crop related materials, Citrus Leaves SRM 1572 and Pine needles SRM 1575 from NIST. A summary of analytical accuracy for this study, established with these reference materials is presented in Table 3. Accuracy estimates are based on the mean performance of either one or both of the laboratories depending on selection and pooling of data for the consolidated database discussed further on.



Table 1. Analytical Precision of Individual Determinations of Total Elemental Concentrations in Soils, Soil Fractions and Crops<sup>1</sup>.

Element	Precision (SD) mg/kg <sup>2</sup>			CV's for soil measurements (%) <sup>4</sup>		
	Soil <sup>3</sup>	Corn	Alfalfa	CV <sub>A</sub>	CV <sub>O</sub>	CV <sub>A</sub> /CV <sub>O</sub>
Al	1500	2.8	2.8	1.86	3.13	0.59
Ba	30	0	0	3.15	13.7	0.23
Be	0	-	-	0	3.95	0
C	940	-	-	7.31	19.5	0.37
Ca	600	290	290	3.41	6.40	0.53
Co	6.0	-	-	29.6	20.8	1.42
Cr	3.2	-	-	3.21	8.83	0.36
Cu	2.4	2.4	2.1	7.23	21.6	0.33
Fe	1400	7.6	7.6	3.26	8.58	0.38
K	690	550	200	3.00	4.30	0.70
La	0.50	-	-	1.13	11.0	0.10
Mg	560	170	170	3.97	8.75	0.45
Mn	27	0.8	1.1	3.44	16.9	0.20
Na	670	4.8	12	3.49	4.98	0.70
Ni	4.3	-	-	7.98	10.8	0.74
P	30	96	96	3.37	12.1	0.28
S	-	125	125	-	-	-
Si	1800	46	46	0.64	3.00	0.21
Sr	13	3.2	3.2	4.21	7.68	0.55
Ti	140	1.1	1.1	3.27	5.43	0.60
V	3.2	-	-	3.32	6.60	0.50
Yb	0.05	-	-	2.27	7.13	0.32
Zn	5.7	3.7	3.9	6.25	12.2	0.51

<sup>1</sup> Calculations are based on analytical precision in either one or the two laboratories conducting analyses, depending on pooling of results, and apply to the consolidated results.

<sup>2</sup> Precision standard deviations are based on 4-15 (typically 5) and 7-29 (typically 14) degrees of freedom for soil and crop analyses, respectively.

<sup>3</sup> These analytical precisions apply to determinations on soils and soil fractions.

<sup>4</sup> CV<sub>A</sub>: analytical coefficient of variation from SD in col. 2 and mean elemental concentration in the typically 40 samples from two horizons from the two fields.

CV<sub>O</sub>: mean overall coefficient of variation (mean of the four CV's per element reported in Tables 5 and 6).

Table 2. Analytical precision of individual determinations of extractable elemental concentrations in soils.

Element	Precision (SD) mg/kg <sup>1</sup>			Analytical CV (CV <sub>A</sub> ) % <sup>2</sup>		
	DTPA	EDTA	HCl	DTPA	EDTA	HCl
Cd	0.029	0.029	0.029	33	25	32
Co	0.05	0.10	0.10	20	4.3	4.8
Cr	0.05	0.32	0.32	31	47	15
Cu	0.076	0.076	0.076	4.8	3.2	4.3
Mn	1.1	10.8	4.8	5.0	9.1	5.9
Ni	0.027	0.16	0.16	6.0	10	11
Pb	0.27	0.27	-	16	14	-
V	-	0.26	0.85	-	14	41
Zn	0.14	0.44	0.44	12	24	15

Element	Overall CV (CV <sub>O</sub> ) % <sup>2</sup>			CV <sub>A</sub> /CV <sub>O</sub>		
	DTPA	EDTA	HCl	DTPA	EDTA	HCl
Cd	55	17	34	0.60	1.50	0.93
Co	41	40	26	0.48	0.11	0.19
Cr	44	39	24	0.48	0.11	0.19
Cu	25	25	22	0.19	0.13	0.20
Mn	34	43	27	0.15	0.21	0.22
Ni	28	34	34	0.21	0.29	0.31
Pb	22	27	-	0.73	0.52	-
V	-	24	46	-	0.56	0.89
Zn	50	35	42	0.24	0.69	0.36

<sup>1</sup> Precision standard deviations are based on 2-12 (typically 8) degrees of freedom. Due to similarities of standard deviations and in order to strengthen estimates, SD's were pooled for Co, Cr, Ni, Zn (EDTA + HCl), Pb (DTPA + EDTA) and Cu, Cd (DTPA + EDTA + HCl).

<sup>2</sup> Analytical coefficient of variation, CV<sub>A</sub> from SD's in columns 2-4 and respective mean extractable concentrations in the typically 40 samples from two horizons from the two fields. Overall coefficient of variation, CV<sub>O</sub> is the mean of typically four CV's for each extractant reported in tables 16-21.

Elements thus controlled for soil analyses include Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Si, Sr, Ti, V and Zn but not Ba, Be, Co, La and Yb for which reference values are unavailable and thus for which no reliability statements can be made. Mean deviations vary from 0% for Fe to 42% for Cu, and are typically 5% indicating excellent performance for all listed elements with the exception of Ni (+37%) and Cu (+42%). Reference material concentrations of Cu are 7, 17, 22, and 61 mg/kg, generally on the low side of the 14-140 mg/kg range observed in soils and fractions. Large systematic error in one laboratory with the 7 mg/kg reference material accounts for much of the 42% error values (which would otherwise be 15% with omission of that data) suggesting reasonable performance to be expected with the soils in this work. As well, in the case of Ni, much of

the systematic error arises from use of the 16 mg/kg reference material (the others contain 26 and 94 mg/kg) on the low side of the Ni level (18-89 mg/kg) in the soils and fractions.

Table 3. Analytical accuracy for determinations of total elemental concentrations established with Reference Materials<sup>1</sup>.

Element	Mean deviation (%) from reference values <sup>2</sup>		Element	Mean deviation (%) from reference values <sup>2</sup>	
	Soils	Crops		Soils	Crops
Al	-4.1	+1.2	Na	+5.4	-18
Ba	-	-4.8	Ni	+37	-
Ca	+1.7	-7.0	P	+7.6	-13
Cr	+17	-	S	-	-17
Cu	+42	+12	Si	-1.5	-
Fe	0.0	-2.8	Sr	-6.0	-6.4
K	-3.2	-3.3	Ti	-5.6	-
Mg	+2.0	-2.8	V	-0.5	-
Mn	+3.6	-9.8	Zn	-1.8	-2.6

<sup>1</sup> Estimates of accuracy are based on performance of either or both laboratories depending on selection and pooling of analytical data for soil and crop samples; these mean estimates are then applicable to the consolidated database.

<sup>2</sup> Mean deviations (%) are deviations from certified or recommended values for CAMNET SO-1, SO-2, SO-3, SO-4 soil reference materials and NIST Citrus Leaves SRM 1572 and Pine needles SRM 1575. Missing values indicate absence of reference values for comparison or non-use of analytical data for that commodity for this study.

Elements controlled for crop analyses include Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, S, Sr and Zn but not Si or Ti for which reference values are unavailable and thus for which no reliability statements can be made. In addition, expected unreliable performance for the determination of Cr and Ni in crop samples as revealed by large systematic errors with the crop reference materials led to rejection of these elements from further consideration. This pertinent example of using a reference material to monitor data quality demonstrates the exclusion of invalid data from the scientific literature. Strictly, analytical results for Ba, Be, Co, La and Yb in soils, and Si and Ti in crops should be omitted as well since no quality controls are available for them; these data have, however, been retained with the proviso that their reliability is unknown. It is noted again that all extractable element data were assessed only in respect of precision and not accuracy as no certified control materials are available for extractable elements in soils.

Analytical results obtained by different laboratories and methods for total elemental concentrations in soil, soil fractions and the three crop tissues were evaluated and processed to yield a table of reliable consolidated data. Data selection criteria were based on precision within each laboratory with the experimental samples and reference materials and accuracy performance with reference materials. Although many elements were determined in only one laboratory, Co, Cu, Mn, Ni, Sr and Zn in soils and Ca, Cu, Fe, Mn, Sr and Zn in corn and alfalfa were measured in both CLBRR and GSC laboratories with generally excellent agreement. For elements determined in two laboratories, usually means of both were selected. Otherwise single or mean determinations from individual laboratories were used. Several elements determined in this work, were eliminated from inclusion in the tables and from further consideration due to unacceptable method performance as demonstrated by use of reference materials. Of all the data considered for this work, outlier rejection rate following use of the stated criteria amounted to 3.7%. Combination of results from different laboratories and methods, with inherently different precisions and systematic errors, will undoubtedly lead to more accurate values, the ultimate objective in generating a reliable database. The end result of this selection procedure was a consolidated database, consisting of individual results for each commodity from each sampling location with associated uncertainties listed in Tables 1 and 2, used for interpretation and discussion of element levels and spatial variabilities.

### Soil Characteristics

Properties taken to characterize the study soils, pH, sand content, silt content, clay content, total carbon, and exchangeable Ca, Mg and K are given in Table 4 for the two horizons in each field. Mean and standard deviations, the latter being a measure of spatial variability are included as well as the results of statistical t tests ( $p = 0.05$ ) resulting from comparisons within and among fields. With both fields, all eight characteristics are significantly different between the Ap and Bg horizons. Within horizon Ap, pH, total carbon, exchangeable Ca and Mg are identical between the two fields, whereas sand, silt and clay contents as well as exchangeable K exhibit significant differences. These observations of differences are interesting in light of the fact that the two fields have identical soil classifications, are in extremely close proximity (separated by about 15 m of highway) but differ in cultivation history. Characteristic properties and their spatial variabilities are also presented diagrammatically in Figures 1A and 1B.



Table 4. Characteristics of Experimental Soils from the two Fields<sup>1</sup>.

Field and horizon	pH	Sand Content %	Silt Content %	Clay Content %
Field 1, Ap	5.1 ± 0.4a	32.5 ± 7.1a	32.8 ± 2.9a	34.7 ± 5.0a
Field 1, Bg	6.1 ± 0.2b	13.9 ± 7.3b	36.0 ± 3.4bc	50.1 ± 7.1b
Field 2, Ap	5.5 ± 0.1c	45.7 ± 6.6c	29.8 ± 2.2d	24.5 ± 5.4c
Field 2, Bg	6.0 ± 0.2b	13.7 ± 4.8b	34.5 ± 6.3ac	51.8 ± 5.0b

	Total carbon %	Exchangeable Cations meq/100 g		
		Ca	Mg	K
Field 1, Ap	2.16 ± 0.34a	6.3 ± 1.6a	4.6 ± 1.8a	0.54 ± 0.22a
Field 1, Bg	0.41 ± 0.09b	12.7 ± 3.5b	9.1 ± 1.8b	0.32 ± 0.10b
Field 2, Ap	2.16 ± 0.42a	7.1 ± 2.1a	3.9 ± 0.8a	0.20 ± 0.04c
Field 2, Bg	0.41 ± 0.09b	14.4 ± 4.9b	10.4 ± 2.2b	0.31 ± 0.05b

<sup>1</sup> All measurements are means ± S.D. for 10 samples from each field/horizon (except 9 samples for carbon determinations on horizon Ap, field 2). Within a column, variables followed by the same letter are not significantly different (t test, p = 0.05).

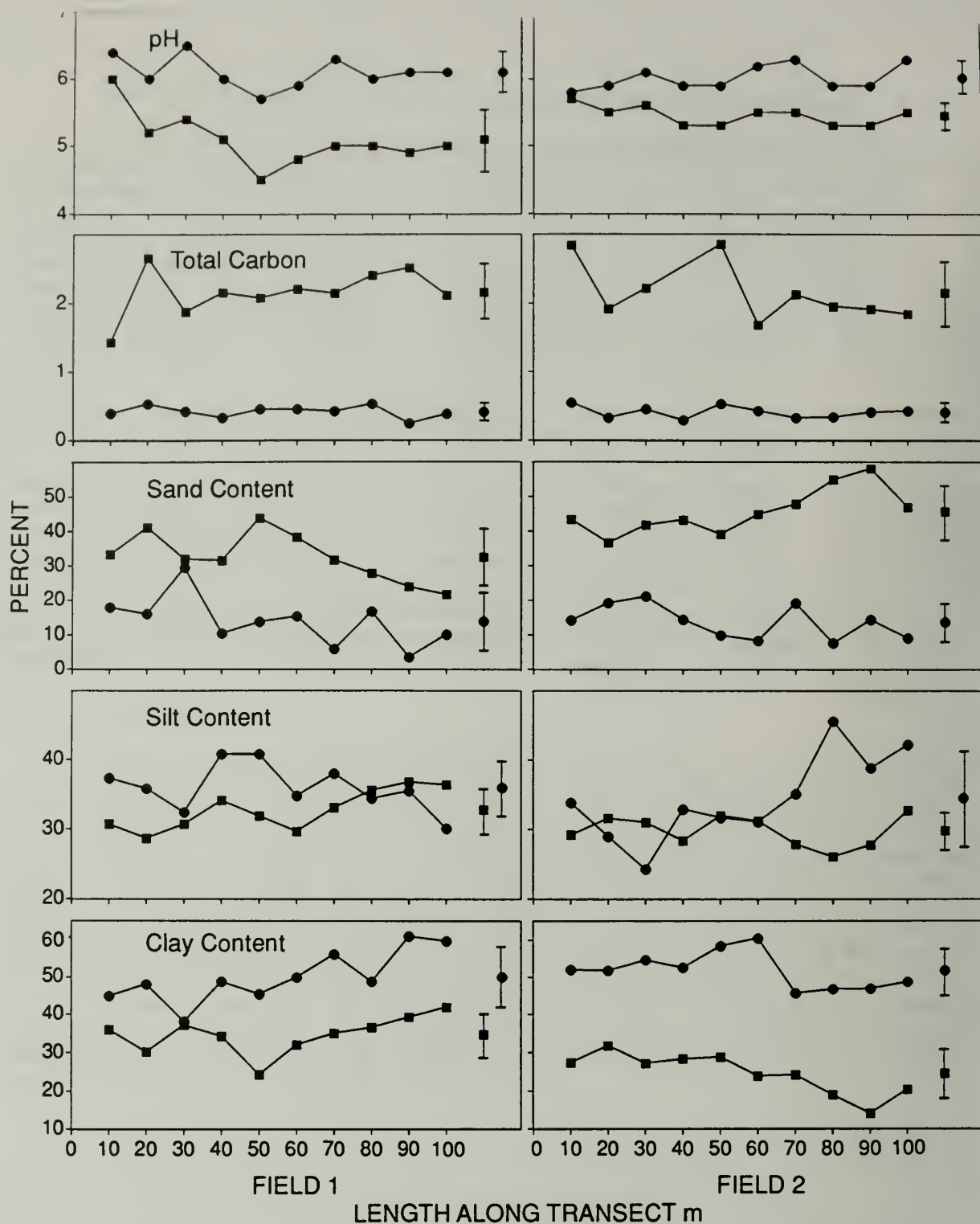


Figure 1A. Characteristic properties, pH (pH units) and carbon, sand, silt and clay contents (%), and their variations in surface (Ap) and subsurface (Bg) horizons along one transect from each of two fields;  $\square$ :Ap,  $\circ$ :Bg. The points at the right of each compartment ( $\bullet \bullet$ ) are means  $\pm$  one standard deviation for the respective horizons.

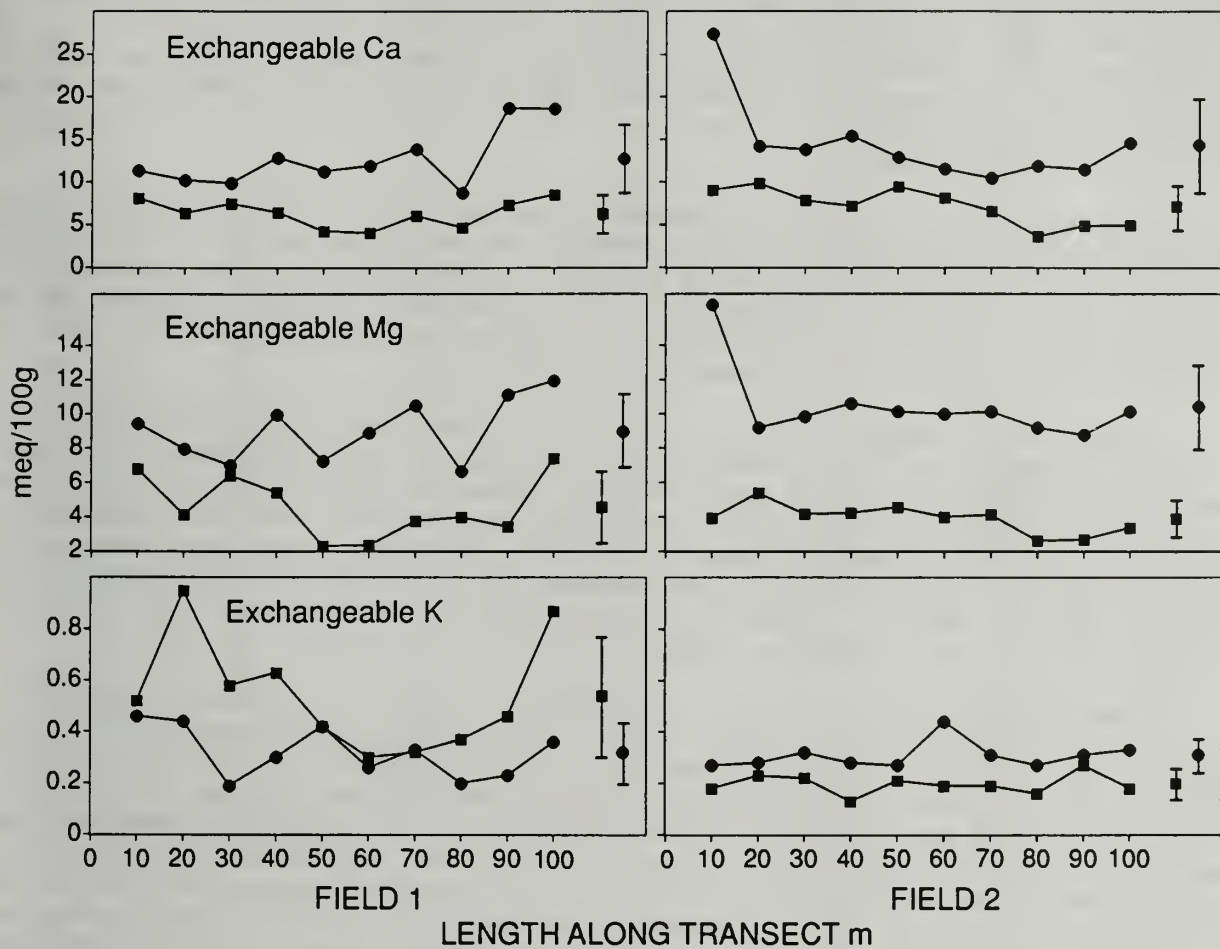


Figure 1B. Characteristic properties (exchangeable cations) and their variations in surface (Ap) and subsurface (Bg) horizons along one transect from each of two fields; •:Ap, •:Bg. The points at the right of each compartment (• •) are means  $\pm$  one standard deviation for the respective horizons.

## Total Elemental Concentrations in Soils

A complete listing of total elemental concentrations for all of the elements in soils of the two fields is presented in Tables 5 and 6. Therein are mean levels over all 10 sampling locations together with standard deviations (SD) and coefficients of variation (CV) for the Ap and Bg horizons. Reference to precisions and precision ratios  $CV_A/CV_O$  in Table 1 where  $CV_A$  and  $CV_O$  are analytical and overall standard deviations, respectively, gives an idea of comparability of the means and indicates that for all elements with the exception of Co for which  $CV_A/CV_O > 1$ , a large part of the variation arises from location to location differences.

Results of statistical treatment are summarized in Table 7 where the mean concentrations are compared between fields and horizons using the t test ( $p = 0.05$ ) with 17-18 degrees of freedom for each of the 88 tests. With the exception of Be in the Ap horizon and Ba and Zn in the Bg horizon for tests between the two fields, and P, Sr, Ti and Yb in field 1 for tests between horizons, all tests (81 out of 88) are highly significant at  $p = 0.01$ .

Mean total element concentrations in surface Ap horizons determined in this work are compared in Table 8 with values reported in the literature. Literature values and means or medians for Canadian (McKeague et al 1979), Ontario (Frank et al 1979; Whitby et al 1978), worldwide (Bowen 1979) and the conterminous United States (Shacklette and Boerngen, 1984). Concentrations determined in this work are generally in very good concordance with literature values, with Al, Ca, Co, Cu, Mg, Mn, Ni, Ti, V and Zn in particularly good agreement and our values for Ba, Cr, Fe and Sr somewhat higher than literature data.

For comparisons of means between fields (Table 7, column 3) where  $T_1$  and  $T_2$  refer to transects from field 1 and 2, respectively, 10 elements, Al, Cr, Fe, La, Mg, Ni, P, Ti, V and Zn, occur at greater concentrations in the Ap horizon of field 1, whereas concentrations of five elements, Be, Ca, Na, Si and Sr are lower in field 1 than field 2. In the Bg horizon, four elemental concentrations, Ba, Mn, P and Zn are greater in field 1. In total, 15 elements in the surface Ap horizon differ significantly in mean concentration between the two fields; only four elements in the subsoil Bg horizon exhibit significant mean concentration differences. Both fields have identical soils but have undergone different long term agricultural practices, as far as known to us, consisting of at least 12 years of continuous corn and hay in fields 1 and 2, respectively. It may then be argued that the highly significant (generally  $p = 0.01$ ) concentration differences in the surface horizon of the two fields may at least be partly the result of different agricultural practices of cropping, fertilization and cultivation. Concentration levels in the Bg horizon of 18 out of 22 elements are similar between the two fields suggesting much less influence of agricultural activity on this lower horizon and retention by the subsoil of more of a pristine nature.

For comparison of mean levels between horizons (Table 7, column 5), for both fields, concentrations are significantly lower in the Ap horizon for Al, Be, Co, Cr, Cu, Fe, K, La, Mg, Mn, Ni, Ti, V, Yb and Zn. In field 1, C, P, Si and Sr are at elevated levels in horizon Ap; in field 2, C, Ca, Na, Si and Sr are at elevated levels in the Ap horizon. Hence, with the exception of three elements,



Table 5. Total Elemental Concentrations (mg/kg) in Soils of Field 1<sup>1</sup>.

Element	Horizon	Minimum	Maximum	Mean	SD	CV(%)
Al	Ap	73600	82100	78260	3140	4.0
	Bg	82600	91600	86850	2840	3.3
Ba	Ap	870	1900	1022	312	30.5
	Bg	900	1100	955	55	5.8
Be	Ap	1.5	1.7	1.61	0.07	4.3
	Bg	1.8	2.1	1.53	0.05	3.3
C	Ap	14300	26600	21620	3440	15.9
	Bg	2400	5300	4140	873	21.1
Ca	Ap	16100	18600	17200	940	5.5
	Bg	14800	21200	17240	2010	11.7
Co	Ap	11	23	15.6	4.0	25.6
	Bg	18	34	26.5	5.2	19.6
Cr	Ap	78	96	89.2	5.4	6.1
	Bg	100	140	120.0	13.3	11.1
Cu	Ap	15	29	22.9	9.0	39.3
	Bg	35	63	45.3	8.2	18.1
Fe	Ap	31300	40900	37610	3080	8.2
	Bg	45600	62200	54130	4520	8.4
K	Ap	19600	22600	21480	840	3.9
	Bg	22000	26000	24590	1230	5.0
La	Ap	26	37	32.2	3.8	11.8
	Bg	40	59	49.0	5.6	11.4
Mg	Ap	9500	12800	11310	1010	8.9
	Bg	15300	20600	18170	1480	8.1
Mn	Ap	500	800	580	92	15.9
	Bg	700	1700	1190	320	26.9
Na	Ap	18000	20200	18880	710	3.8
	Bg	15900	21000	17880	1470	8.2
Ni	Ap	34	46	41.0	4.2	10.2
	Bg	54	87	72.7	9.6	13.2
P	Ap	900	1200	1080	103	9.5
	Bg	700	1200	960	135	14.1
Si	Ap	278800	306300	289280	8340	2.9
	Bg	254900	290900	264710	10490	4.0
Sr	Ap	288	342	317	21	6.6
	Bg	248	353	284	33	11.6
Ti	Ap	4100	4400	4250	97	2.3
	Bg	4200	5800	4570	455	10.0
V	Ap	75	99	87.8	6.3	7.2
	Bg	105	120	113.5	5.8	5.1
Yb	Ap	1.9	2.3	2.06	0.14	6.8
	Bg	2.0	2.7	2.26	0.23	10.2
Zn	Ap	71	95	83.8	7.5	8.9
	Bg	85	151	119.6	19.2	16.1

<sup>1</sup> Based on analyses of 10 samples from one 100 m transect.

Table 6. Total Elemental Concentrations (mg/kg) in Soils of Field 2<sup>1</sup>.

Element	Horizon	Minimum	Maximum	Mean	SD	CV(%)
Al	Ap	69400	74600	71910	1600	2.2
	Bg	81000	88400	84830	2550	3.0
Ba	Ap	830	1300	912	148	16.2
	Bg	880	950	914	22	2.4
Be	Ap	1.5	1.6	1.95	0.09	4.6
	Bg	1.9	2.1	1.96	0.07	3.6
C	Ap	16900	28600	21560	4250	19.7
	Bg	2900	5500	4090	872	21.3
Ca	Ap	18400	19400	18690	340	1.8
	Bg	15000	18900	17310	1150	6.6
Co	Ap	9	21	13.4	3.3	24.6
	Bg	20	32	25.6	3.4	13.3
Cr	Ap	56	80	70.2	7.5	10.7
	Bg	110	130	119.0	8.8	7.4
Cu	Ap	13	24	19.4	3.5	18.0
	Bg	38	54	45.2	5.0	11.1
Fe	Ap	24100	33600	29290	3300	11.3
	Bg	46200	56300	51000	3240	6.4
K	Ap	20100	22000	21160	670	3.2
	Bg	22700	26500	24720	1260	5.1
La	Ap	24	32	27.3	2.4	8.8
	Bg	39	60	50.7	6.1	12.0
Mg	Ap	7800	10800	9210	1010	11.0
	Bg	15700	19500	17670	1240	7.0
Mn	Ap	500	700	540	73	13.5
	Bg	700	1000	850	97	11.4
Na	Ap	20200	22900	21510	900	4.2
	Bg	17200	19100	18510	680	3.7
Ni	Ap	26	36	31.3	3.4	10.9
	Bg	64	81	70.7	6.3	8.9
P	Ap	600	900	733	100	13.6
	Bg	700	900	790	88	11.1
Si	Ap	293000	325100	307130	9680	3.2
	Bg	261900	278300	269220	5140	1.9
Sr	Ap	327	389	356	21	5.9
	Bg	260	323	287	19	6.6
Ti	Ap	3700	4300	3910	185	4.7
	Bg	4100	4800	4400	205	4.7
V	Ap	61	84	73.8	7.2	9.8
	Bg	100	120	110.0	4.7	4.3
Yb	Ap	2.0	2.1	2.06	0.05	2.4
	Bg	1.9	2.7	2.41	0.22	9.1
Zn	Ap	47	70	57.4	8.0	13.9
	Bg	87	118	101.1	10.1	10.0

<sup>1</sup> Based on analyses of 10 samples (except 9 from horizon Ap) from one 100 m transect.

Table 7. Statistical Comparisons of Total Elemental Concentrations.

Element	Horizon	Comparison of		
		Means Between fields <sup>1</sup>	Variances Between fields <sup>2</sup>	Means Between horizons <sup>3</sup>
Al	Ap	T1 > T2	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : Ap < Bg
Ba	Ap	NS	T1 > T2	T <sub>1</sub> : NS
	Bg	T1 > T2	T1 > T2	T <sub>2</sub> : NS
Be	Ap	T1 < T2	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : Ap < Bg
C	Ap	NS	NS	T <sub>1</sub> : Ap > Bg
	Bg	NS	NS	T <sub>2</sub> : Ap > Bg
Ca	Ap	T1 < T2	T1 > T2	T <sub>1</sub> : NS
	Bg	NS	NS	T <sub>2</sub> : Ap > Bg
Co	Ap	NS	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : Ap < Bg
Cr	Ap	T1 > T2	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : Ap < Bg
Cu	Ap	NS	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : Ap < Bg
Fe	Ap	T1 > T2	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : Ap < Bg
K	Ap	NS	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : Ap < Bg
La	Ap	T1 > T2	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : Ap < Bg
Mg	Ap	T1 > T2	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : Ap < Bg
Mn	Ap	NS	NS	T <sub>1</sub> : Ap < Bg
	Bg	T1 > T2	T1 > T2	T <sub>2</sub> : Ap < Bg
Na	Ap	T1 < T2	NS	T <sub>1</sub> : NS
	Bg	NS	T1 > T2	T <sub>2</sub> : Ap > Bg
Ni	Ap	T1 > T2	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : Ap < Bg
P	Ap	T1 > T2	NS	T <sub>1</sub> : Ap > Bg
	Bg	T1 > T2	NS	T <sub>2</sub> : NS
Si	Ap	T1 < T2	NS	T <sub>1</sub> : Ap > Bg
	Bg	NS	T1 > T2	T <sub>2</sub> : Ap > Bg
Sr	Ap	T1 < T2	NS	T <sub>1</sub> : Ap > Bg
	Bg	NS	NS	T <sub>2</sub> : Ap > Bg
Ti	Ap	T1 > T2	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	T1 > T2	T <sub>2</sub> : Ap < Bg
V	Ap	T1 > T2	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : Ap < Bg
Yb	Ap	NS	T1 > T2	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : Ap < Bg
Zn	Ap	T1 > T2	NS	T <sub>1</sub> : Ap < Bg
	Bg	T1 > T2	NS	T <sub>2</sub> : Ap < Bg

Table 7. (contd.)

- <sup>1</sup> Based on t tests ( $p = 0.05$ ) with 17-18 degrees of freedom.  $T_1$  and  $T_2$  refer to transects from field 1 and 2 respectively. NS: not significantly different. With the exception of Be (Ap) and Ba, Zn (Bg), all significantly different means are also so at  $p = 0.01$ .
- <sup>2</sup> Based on F tests ( $p = 0.05$ ) with 9/8 or 9/9 degrees of freedom. The following are also significantly different at  $p = 0.01$ : Ca(Ap), Yb(Ap) and Mn(Bg).
- <sup>3</sup> Based on t tests ( $p = 0.05$ ) with 17-18 degrees of freedom. NS: not significantly different. With the exception of P, Sr, Ti and Yb in  $T_1$ , all significantly different means are also so at  $p = 0.01$ .

Table 8. Comparison of mean total element concentrations (mg/kg) determined in this work with values reported in the literature for Canadian and other soils.

Element	Mean concentration in surface Ap horizons in the 2 fields - this work <sup>1</sup>	Mean/median concentrations reported in the literature				
		A <sup>2</sup>	B <sup>3</sup>	C <sup>4</sup>	D <sup>5</sup>	E <sup>6</sup>
Al	75100	62000	-	-	71000	-
Ba	970	-	-	-	500	580
Be	1.8	-	-	-	0.3	0.92
Ca	17950	15000	-	-	15000	-
Co	14.5	21	5	-	8	9.1
Cr	80	45	14	53	70	54
Cu	21	22	25	19	30	25
Fe	33450	26000	14500	-	40000	-
Mg	10260	8200	-	-	5000	-
Mn	560	544	530	-	1000	550
Ni	36	22	16	20	50	19
Sr	337	207	-	-	250	240
Ti	4080	4400	-	-	5000	2900
V	81	-	-	-	90	80
Zn	71	77	54	88	90	60

<sup>1</sup> Means of mean values for fields 1 and 2 listed in Tables 5 and 6.

<sup>2</sup> Means for Canadian soils (McKeague et al 1979).

<sup>3</sup> Means in many Ontario soils (Frank et al 1976).

<sup>4</sup> Means in Ap horizons of soils in six agricultural watersheds in Southwestern Ontario (Whitby et al 1978).

<sup>5</sup> Medians for soils from various worldwide locations (Bowen 1979).

<sup>6</sup> Mean levels for soils of the conterminous United States (Schacklette and Boerngen, 1984).



P, Ca and Na, between horizon comparisons of mean elemental concentrations are identical. A visual presentation of the foregoing discussions may be had by reference to the points representing means  $\pm$  standard deviations included in figures 2-5.

A comparison of variances of mean concentrations between fields is presented in column 4 of Table 7. These are based on F tests ( $p = 0.05$ ) with 9/8 or 9/9 degrees of freedom. Of 44 comparisons, only eight are significantly different indicating generally identical elemental variation magnitude within each field. In all eight cases, (seven elements) the variances in field 1 consistently exceed those in field 2 with Ba, Ca and Yb in horizon Ap and Ba, Mn, Na, Si and Ti in horizon Bg exhibiting the significant differences. Variances for Ca, Yb and Mn are also highly significant at  $p = 0.01$ . Aside from a (statistical) sampling effect, differences for the minor elements Ba, Mn and Yb and the major ones Ca and Na may be ascribable to differences in cultivation, specifically to non-uniform contributions from fertilizers and other amendments. Differences in variations of Si and Ti concentrations in the subsoil cannot be explained by cultivation factors and may in fact arise from variability inherent in the soil.

#### Variability of Total Elemental Concentrations within Transects

Indications of the within transect variability of total elemental concentrations can be surmised from Figures 2 to 5 and Table 9. Concentrations at each of the 10 individual sampling locations are plotted for Al, Ba, Ca, Co and Cr in Figure 2, Cu, Fe, K, La and Mg in Figure 3, Mn, Na, Ni, P and Si in Figure 4, and Sr, Ti, V, Yb and Zn in Figure 5. In each figure, data are presented for each horizon in each field and an indication of typical analytical uncertainty is depicted by error bars on the first or second points of each plot. Points at the extreme right of each plot depict mean  $\pm$  one standard deviation over all 10 locations for comparison. Visual inspection of the plots in Figures 2 to 5 can conveniently give indications of the following items: (a) concentration variations among sampling locations for each horizon and field based primarily on the scatter of individual plotted points but also on the mean  $\pm$  SD points, (b) comparison of variability and mean levels between horizons, (c) variability between fields for each horizon, (d) comparison of mean levels between fields and (e) concentration trends along each transect (horizon and field). Items c, d, and means referred to in b have been presented in Table 7 and discussed.

Variability among sampling locations and concentration trends along the transects are presented in Table 9 and summarized in Table 10. To establish the significance of variation among sampling locations or positions, t-tests were conducted (visual quantitative) between all pairs of points, namely 45 possible combinations of ten points taken two at a time for each element. This was done by superimposing movable error bars to each pair of points designed to detect  $p = 0.05$  overlap. Presence of overlaps indicated no significant differences, denoted NS in the Table, whereas lack of overlap in many of the pairs indicated significant differences denoted S in the Table. Out of 42 element/horizon combinations (Be has been omitted due to poor analytical behaviour), 20/42 or about one half exhibit significant variation among position in field 1. Significant variations with position are shown by Al, Ba, C, Cu, La, P, Si and Yb (8 elements) in the Ap horizon and by Ca, Cr, Cu, Fe, La, Mg, Mn, Na, Ni, P, Si, Sr, Yb and Zn (14 elements) in the Bg horizon. Logically, fewer elements

exhibit significant concentration variability in the cultivated Ap horizon than in the subsoil. In field 2, in 9/42 situations significant inter-position variation is shown by four elements, C, La, P and Si in the Ap horizon, and four elements, La, Mn, P and Yb in the Bg horizon. Elements common to the two fields exhibiting significant variation among position are C, La, P and Si in the Ap horizon; and La, Mn, P and Yb in the Bg horizon.

General trends of concentration with position along the transects are also indicated in Table 8 as increasing, decreasing, no direction and the presence of one or more maximum or minimum and are also summarized in Table 10. Within field 1, nine elements, Al, Ca, Co, K, Mn, P, Si, Sr, and Zn show some trend in the two horizons, with seven occurrences in Ap versus five in Bg. Similarly, within field 2, nine elements, C, Ca, Mg, Ni, Si, Sr, Ti, V and Zn exhibit some trend in the two horizons with seven occurrences in Ap versus three in Bg. Elements common to the two fields exhibiting significant trends with position are Si and Sr in the Ap horizon.

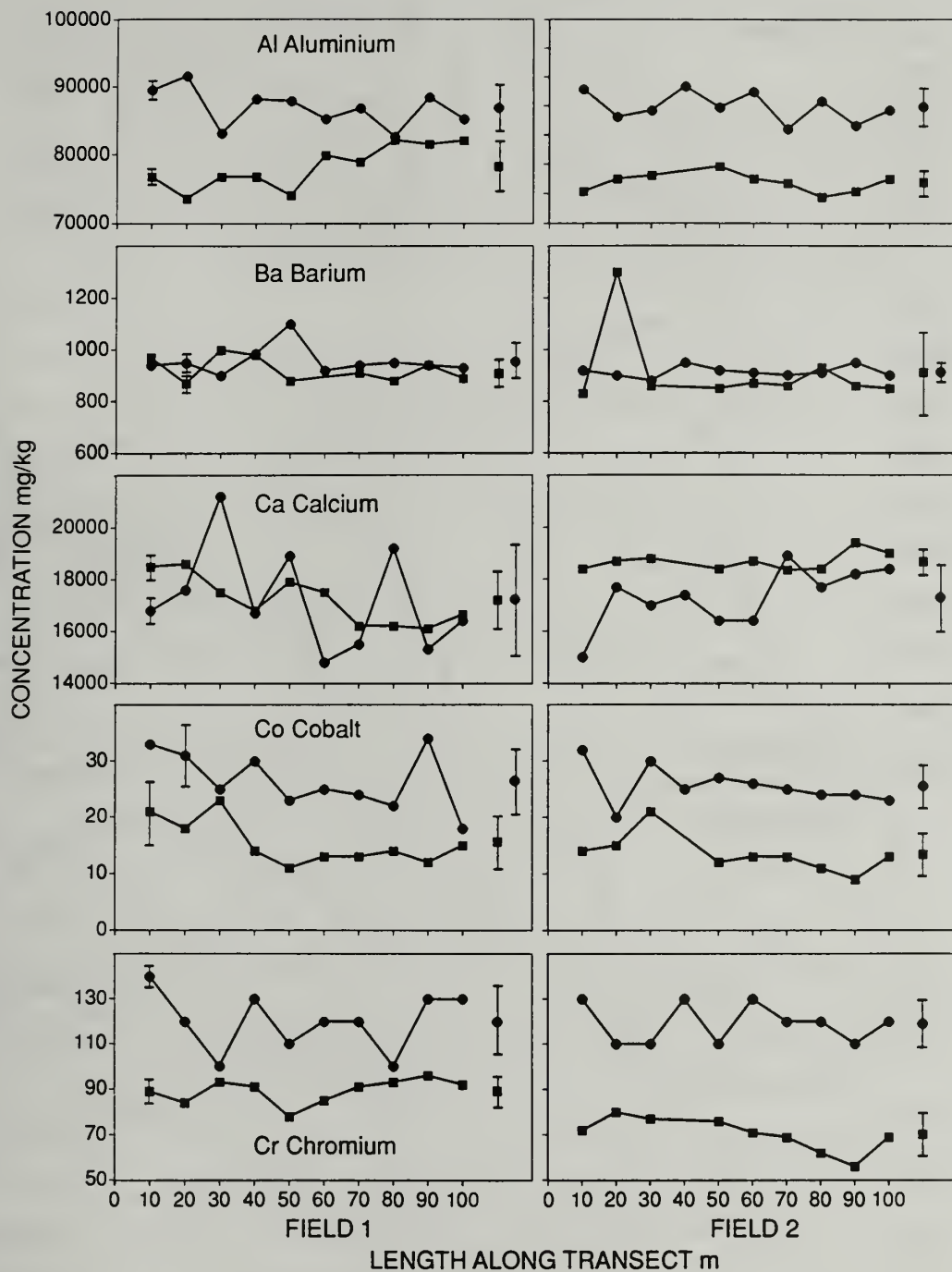


Figure 2. Total concentrations (mg/kg) of Al, Ba, Ca, Co and Cr and their variations in surface (Ap) and subsurface (Bg) horizons along one transect in each of two field, •:Ap, •:Bg. Typical one standard deviations of individual determinations (analytical precision) are indicated by error bars on first or second points of each plot. The points at the right of each compartment (• •) are means  $\pm$  one standard deviation for the respective horizons. The absence of an error bar indicates that the uncertainty is within the dimensions of the point.

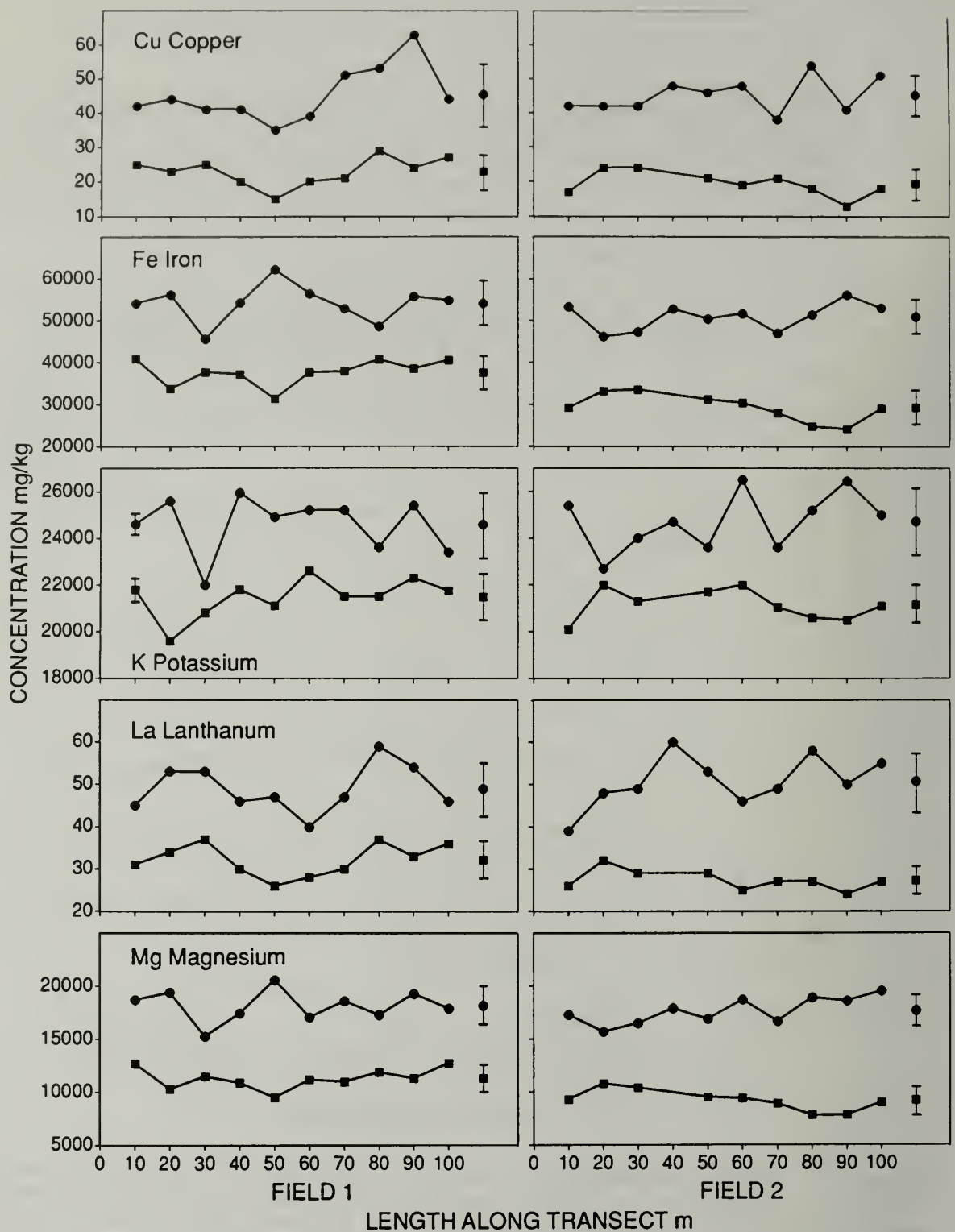


FIGURE 3. Total concentrations (mg/kg) of Cu, Fe, K, La and Mg and their variations in surface (Ap) and subsurface (Bg) horizons along one transect in each of two fields; •:Ap, •:Bg. Refer to caption to figure 2 for details.



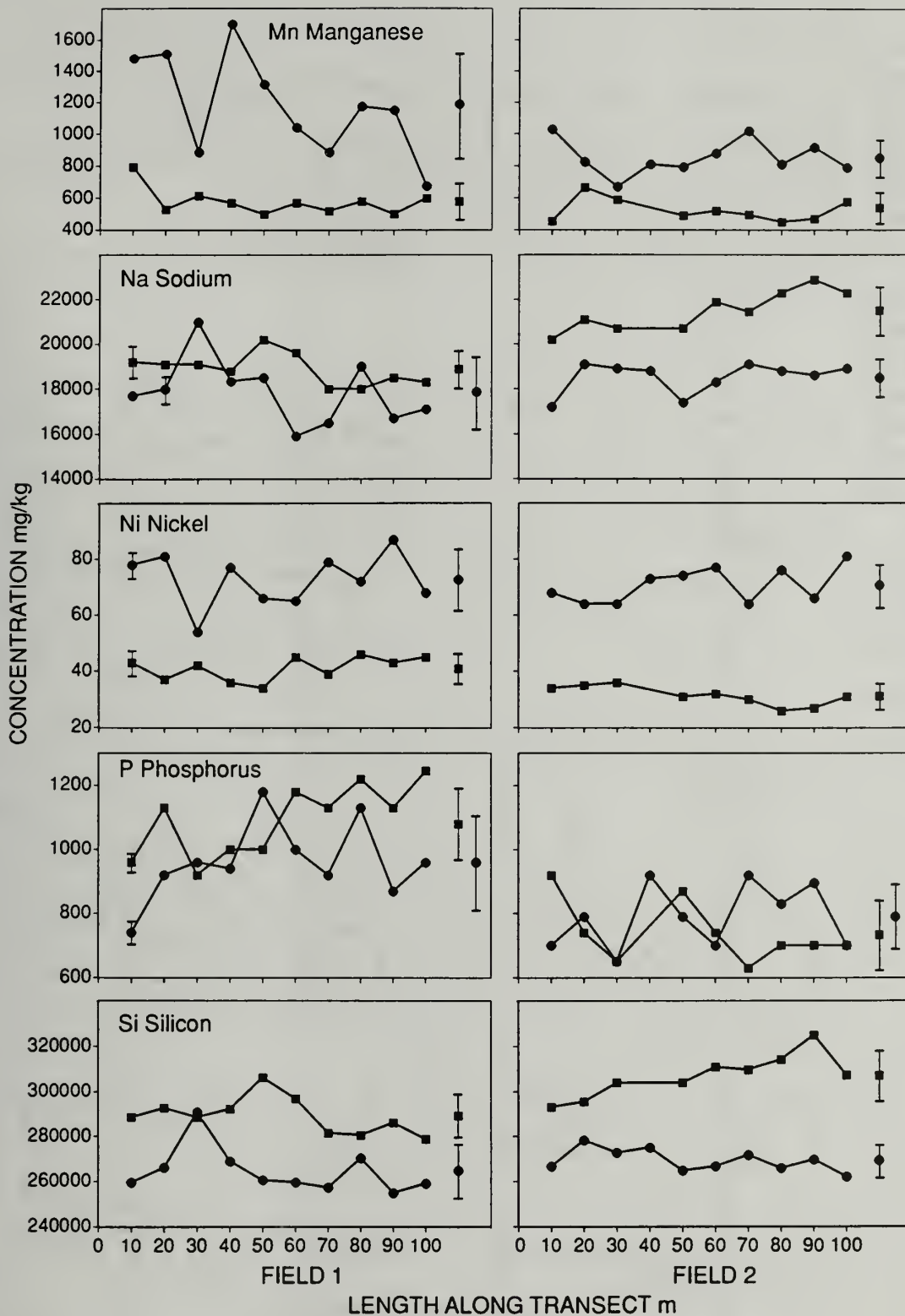


FIGURE 4. Total concentrations (mg/kg) of Mn, Na, Ni, P and Si and their variations in surface (Ap) and subsurface (Bg) horizons along one transect in each of two fields;  $\square$ :Ap,  $\bullet$ :Bg. Refer to caption to figure 2 for details.

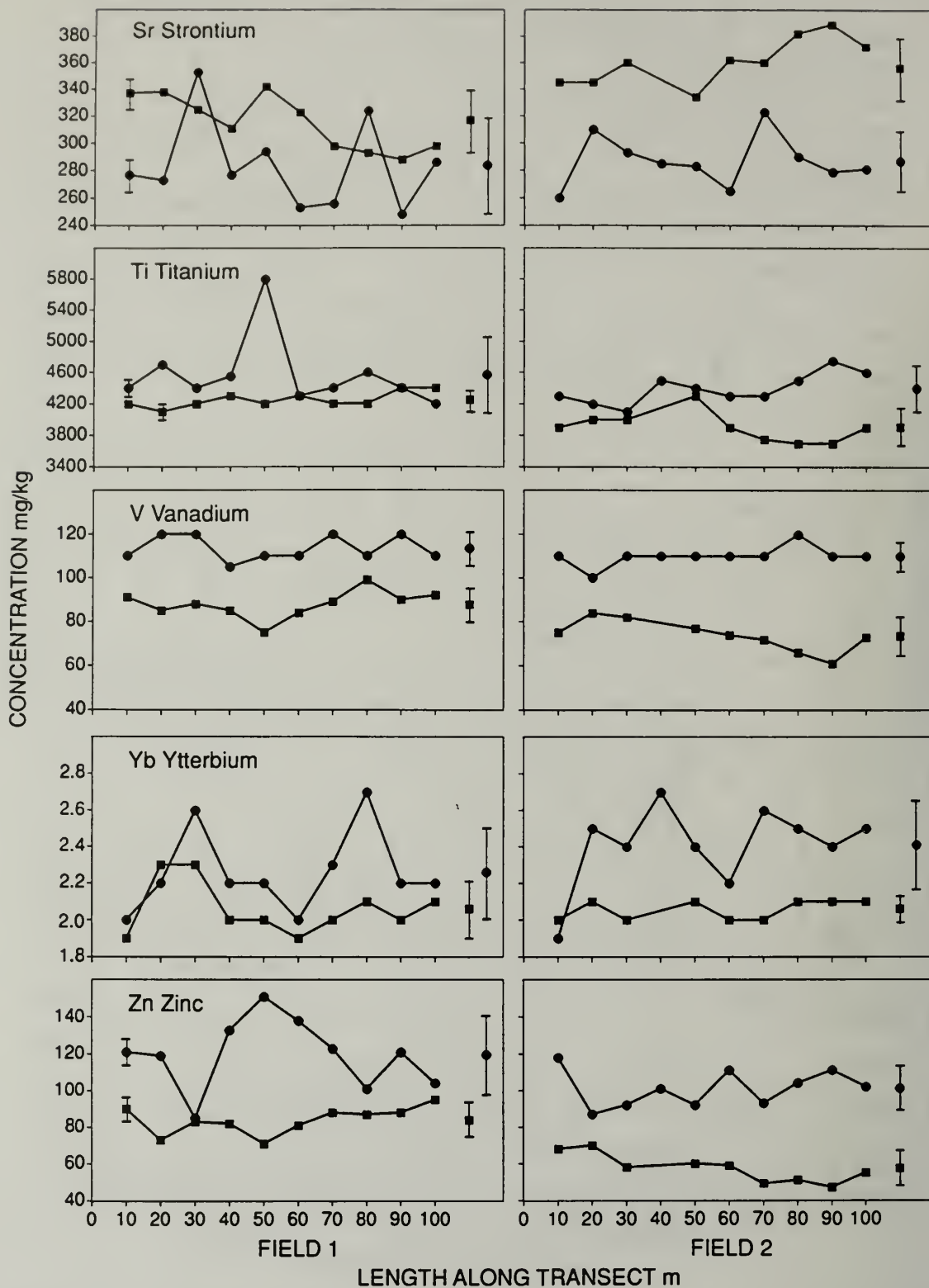


FIGURE 5. Total concentrations (mg/kg) of Sr, Ti, V, Yb and Zn and their variations in surface (Ap) and subsurface (Bg) horizons along one transect in each of two fields; \*:Ap, •:Bg. Refer to caption to figure 2 for details.

Table 9. Variability of Total Elemental Concentrations in Soil of the two Fields.

Element	Horizon	Field 1		Field 2	
		Significant variation among position <sup>1</sup>	Trend with Position <sup>2</sup>	Significant variation among position <sup>1</sup>	Trend with Position <sup>2</sup>
Al	Ap	S	↑	NS	N
	Bg	NS	N	NS	N
Ba	Ap	S	N	NS	N
	Bg	NS	N	NS	N
C	Ap	S	N	S	↓
	Bg	NS	N	NS	N
Ca	Ap	NS	↓	NS	N
	Bg	S	N	NS	↑
Co	Ap	NS	↓	NS	N
	Bg	NS	↓	NS	N
Cr	Ap	NS	N	NS	N
	Bg	S	N	NS	N
Cu	Ap	S	N	NS	N
	Bg	S	↑	NS	N
Fe	Ap	NS	N	NS	N
	Bg	S	N	NS	N
K	Ap	NS	↑	NS	N
	Bg	NS	N	NS	N
La	Ap	S	N	S	N
	Bg	S	N	S	N
Mg	Ap	NS	N	NS	N
	Bg	S	N	NS	↑
Mn	Ap	NS	N	NS	N
	Bg	S	↓	S	N
Na	Ap	NS	N	NS	N
	Bg	S	N	NS	N
Ni	Ap	NS	N	NS	↓
	Bg	S	N	NS	N
P	Ap	S	↑	S	N
	Bg	S	N	S	N
Si	Ap	S	M	S	↑
	Bg	S	M	NS	N
Sr	Ap	NS	↓	NS	↑
	Bg	S	N	NS	N
Ti	Ap	NS	N	NS	↓
	Bg	NS	N	NS	↑
V	Ap	NS	N	NS	↓
	Bg	NS	N	NS	N
Yb	Ap	S	N	NS	N
	Bg	S	N	S	N
Zn	Ap	NS	N	NS	↓
	Bg	S	M	NS	N

<sup>1</sup> Based on visual t tests of plotted data among the typically 10 positions.

<sup>2</sup> General trend of concentrations along transect from 10 to 100 m is depicted as ↑: increase; ↓: decrease; N: No Trend; M: one or more maxima/minima.

Table 10. Summary of behaviour of total elemental concentrations in soil of two fields based on evaluation of graphical plots.

Horizon	Field 1		Field 2	
	Elements with significant variation among position	trend with position	Elements with significant variation among position	trend with position
Ap	Al, Ba, C Cu, La, P Si, Yb	Al, Ca, Co K, P, Si Sr	C, La, P Si	C, Ni, Si, Sr Ti, V, Zn
Bg	Ca, Cr, Cu, Fe La, Mg, Mn Na, Ni, P, Si Sr, Yb, Zn	Co, Cu, Mn Si, Zn	La, Mn, P Yb	Ca, Mg, Ti
Common elements to Fields 1 and 2 with significant Variation among position				
Ap	C, La, P, Si		Si, Sr	
Bg	La, Mn, P, Yb			

## Total Elemental Concentrations in Soil Fractions

Detailed compilations of mean total elemental concentrations in sand, silt and clay fractions from field 1 and 2 are presented in Tables 11 and 12, respectively. Analyses were carried out on fractions from soils from three of the ten sampling sites within each field located at 20, 50 and 80 m and 10, 50 and 70 m along transects in fields 1 and 2 respectively. Included are standard deviations and CV's. Comparison of the latter, equivalent to overall  $CV_0$ 's, with analytical precision  $CV_A$ 's listed in Table 1 gives an indication of variation among position within the transect, and suggests that generally, the reported CV's reflect small concentration variations within the fields. This information is diagrammatically presented in Figures 6-9 permitting a quick visual comparison of concentrations among fractions, locations and fields. Elemental concentration data for whole soil samples from the corresponding three locations in each field are included for comparison. Typical one standard deviations of individual determinations (analytical precision, identical to precisions listed in column 2 of table 1) are indicated by points within each plot. Generally, concentrations were highest in the clay fractions followed by levels in silt and sand for all elements with the exception of Ca, K, Mn, Na, Si and Sr which exhibited the reverse trend or no trend at all. Even though data are on materials prepared from soil from only three locations from each field, quite tight agreement of concentrations among sampling position is evidenced by the low CV's.

Statistical calculations were carried out using the t-test at 0.05 and 0.01 significance levels comparing mean concentrations between fields and horizons for each of the sand, silt and clay fractions and are presented in Table 13. Summaries of these statistical considerations are presented in Tables 14-16. With respect to comparisons between the fields (Table 14), a total of 15 and 4 significant differences were observed in the Ap and Bg horizons, respectively, with many of these occurring in the silt fraction. In most instances, within the same fraction and horizon, concentrations in field 1 were greater than those in field 2. With respect to comparisons between horizon (Table 15), overwhelmingly, elemental concentrations in fractions from the Ap horizon were lower than those in the Bg horizon, with a somewhat larger number of significant differences occurring in field 2. A final statistical summary tabulation for elements with identical behaviour in both fields is given in Table 16. These common elements are Al, Be, Ca, Co, Fe, La, Mg, Mn, Na, P, Sr and Yb with often different elements represented in the different fractions. Only Ca, Mg, Mn and P have more than one fraction in common, with Mn and P represented in all three.



Table 11. Total Elemental Concentrations (mg/kg) in Sand, Silt and Clay Fractions from Soil of Field 1<sup>1</sup>.

Element	Horizon	SAND			SILT			CLAY		
		Mean	SD	CV%	Mean	SD	CV%	Mean	SD	CV%
Al	Ap	71600	1610	2.2	65830	2670	4.1	99530	1380	1.4
	Bg	72870	3000	4.1	73930	1360	1.8	95130	1140	1.2
Ba	Ap	887	15	1.7	837	15	1.8	767	23	3.0
	Bg	967	42	4.3	910	35	3.8	1150	477	41.5
Be	Ap	1.50	0.10	6.7	1.50	0.00	0	1.80	0.17	9.4
	Bg	1.93	0.21	10.9	1.70	0.00	0	2.07	0.06	2.9
Ca	Ap	23070	860	3.7	20900	350	1.7	4070	150	3.7
	Bg	20970	1850	8.8	25330	1500	5.9	8070	290	3.6
Co	Ap	17.3	1.5	8.7	21.0	2.0	9.5	31.3	6.4	20.4
	Bg	41.0	10.6	25.9	21.0	2.0	9.5	35.7	5.5	15.4
Cr	Ap	37.0	6.0	16.2	56.3	3.1	5.5	143.3	5.8	4.0
	Bg	70.7	26.1	36.9	52.3	9.1	17.4	140.0	10.0	7.1
Cu	Ap	42.0	19.7	46.9	32.0	3.6	11.3	237.7	166.5	70.0
	Bg	108.7	120.7	111.0	30.3	10.3	34.0	169.7	81.7	48.1
Fe	Ap	20830	2940	14.1	23300	1650	7.1	70130	2830	4.0
	Bg	40170	13690	34.1	27770	1070	3.9	69270	5190	7.5
K	Ap	20370	310	1.5	21930	900	4.1	22730	2230	9.8
	Bg	23370	310	1.3	24000	850	3.5	26200	1470	5.6
La	Ap	18.0	2.0	11.1	31.0	2.0	6.5	53.7	10.4	19.4
	Bg	43.0	8.9	20.7	33.3	5.5	16.5	72.3	19.7	27.2
Mg	Ap	6670	510	7.6	7970	290	3.6	23200	530	2.3
	Bg	10100	3210	31.8	9930	500	5.0	27330	1250	4.6
Mn	Ap	433	58	13.4	533	58	10.9	467	58	12.4
	Bg	1300	283	21.8	667	58	8.7	700	0	0
Na	Ap	26170	510	1.9	24770	60	0.2	6730	120	1.8
	Bg	24500	2990	12.2	28100	350	1.2	11900	360	3.0
Ni	Ap	17.7	4.0	22.6	24.7	0.6	2.4	77.7	4.0	5.1
	Bg	43.0	15.1	35.1	23.7	3.5	14.8	89.3	11.2	12.5
P	Ap	1000	265	26.5	767	115	15.0	5100	520	10.2
	Bg	1833	379	20.7	1167	58	5.0	2867	208	7.3
Si	Ap	342200	8850	2.6	321300	10380	3.2	220900	3120	1.4
	Bg	309500	22840	7.4	344400	29090	8.4	229800	2820	1.2
Sr	Ap	477	13	2.7	405	10	2.5	101	8	7.9
	Bg	403	50	12.4	439	23	5.2	167	11	6.6
Ti	Ap	2400	173	7.2	4430	252	5.7	6670	702	10.5
	Bg	2900	529	18.2	4130	252	6.1	5600	755	13.5
V	Ap	50.3	10.0	19.9	63.7	5.5	8.6	136.7	5.6	4.1
	Bg	108.0	33.1	30.6	67.7	4.2	6.2	120.0	10.0	8.3
Yb	Ap	1.63	0.15	9.2	3.03	0.12	4.0	1.53	0.21	13.7
	Bg	2.40	0.10	4.2	3.00	0.36	12.0	2.17	0.55	25.3
Zn	Ap	34.3	5.0	14.6	49.7	2.1	4.2	241.3	44.7	18.5
	Bg	82.7	35.9	43.4	52.3	2.5	4.8	205.0	37.8	18.4

<sup>1</sup> Each concentration is the mean of analyses of three samples, one from each of three locations at 20, 50 and 80 m along the transect.

Table 12. Total Elemental Concentrations (mg/kg) in Sand, Silt and Clay Fractions from Soil of Field 2<sup>1</sup>.

Element	Horizon	SAND			SILT			CLAY		
		Mean	SD	CV%	Mean	SD	CV%	Mean	SD	CV%
Al	Ap	66330	2190	3.3	66870	1700	2.5	100600	1900	1.9
	Bg	68130	2120	3.1	71630	810	1.1	98630	2580	2.6
Ba	Ap	927	29	3.1	897	15	1.7	683	6	0.9
	Bg	865	7	0.8	1000	176	17.6	867	12	1.4
Be	Ap	1.43	0.06	4.2	1.40	0.00	0	1.50	0.0	0
	Bg	1.87	0.06	3.2	1.70	0.00	0	1.97	0.06	3.0
Ca	Ap	21030	1030	4.9	20700	700	3.4	4470	1070	23.9
	Bg	19870	1720	8.7	23970	860	3.6	7500	1450	19.3
Co	Ap	15.7	0.6	3.8	16.7	1.2	7.2	22.7	1.5	6.6
	Bg	37.0	7.9	21.4	22.0	1.0	4.5	28.7	0.6	2.1
Cr	Ap	33.3	3.1	9.3	48.3	2.9	6.0	136.7	5.6	4.1
	Bg	74.3	21.0	28.3	61.7	1.5	2.4	140.0	10.0	7.1
Cu	Ap	14.0	1.0	7.1	16.3	3.1	19.0	140.0	10.0	7.1
	Bg	38.7	12.3	31.8	18.3	3.2	17.5	95.3	0.6	0.6
Fe	Ap	18870	910	4.8	20570	680	3.3	65030	3080	4.7
	Bg	39430	8640	21.9	27930	380	1.4	67800	1850	2.7
K	Ap	21070	570	2.7	24100	700	2.9	21570	1180	5.5
	Bg	20900	800	3.8	22700	2180	9.6	25800	1040	4.0
La	Ap	16.0	1.7	10.6	25.3	1.2	4.7	45.0	1.7	3.8
	Bg	40.0	5.2	13.0	31.3	2.9	9.3	52.7	9.3	17.6
Mg	Ap	5600	760	13.6	7530	290	3.9	22970	1250	5.4
	Bg	10270	2010	19.6	10030	670	6.7	27000	1040	3.9
Mn	Ap	400	0	0	467	58	12.4	400	0	0
	Bg	1230	320	26.0	767	115	15.0	630	58	9.2
Na	Ap	26870	830	3.1	27300	1020	3.7	6970	720	10.3
	Bg	21900	2150	9.8	26600	1440	5.4	11300	1180	10.4
Ni	Ap	17.7	3.1	17.5	19.3	0.6	3.1	72.0	3.6	5.0
	Bg	50.0	11.1	22.2	24.3	1.5	6.2	84.7	1.2	1.4
P	Ap	700	173	24.7	467	58	12.4	4670	153	3.3
	Bg	1400	265	18.9	1030	58	5.6	2630	153	5.8
Si	Ap	343000	2820	0.8	339600	4840	1.4	224200	7140	3.2
	Bg	283000	16720	5.9	315200	6140	1.9	236100	2100	0.9
Sr	Ap	478	19	4.0	409	11	2.7	113	6	5.3
	Bg	410	51	12.4	430	24	5.6	163	21	12.9
Ti	Ap	2133	321	15.0	4367	153	3.5	7300	265	3.6
	Bg	2833	321	11.3	4067	115	2.8	5230	153	2.9
V	Ap	47.7	1.5	3.1	53.3	1.2	2.3	126.7	5.8	4.6
	Bg	108.0	13	12.0	71.7	1.5	2.1	113.3	5.8	5.1
Yb	Ap	1.57	0.31	19.7	2.67	0.15	5.6	1.27	0.06	4.7
	Bg	2.27	0.23	10.1	2.87	0.21	7.3	1.57	0.32	20.4
Zn	Ap	35.0	8.72	24.9	40.7	1.5	3.7	190.0	36.1	19.0
	Bg	71.0	21.9	30.8	53.0	1.7	3.2	156.7	25.2	16.1

<sup>1</sup> Each concentration is the mean of analyses of three samples, one from each of three locations at 10, 50 and 70 m along the transect (except data for Ba in sand from horizon Bg where only two samples were available).

Table 13. Statistical comparisons of total elemental concentrations in sand, silt and clay soil fractions<sup>1</sup>.

Element	Horizon	Sand		Silt		Clay	
		fields <sup>2</sup>	horizons <sup>3</sup>	Comparison of means between fields <sup>2</sup> horizons <sup>3</sup>		fields <sup>2</sup>	horizons <sup>3</sup>
Al	Ap	$T_1 > T_2$	$T_1$ :NS	NS	$T_1$ :Ap<Bg	NS	$T_1$ :Ap>Bg
	Bg	NS	$T_2$ :NS	NS	$T_2$ :Ap<Bg	NS	$T_2$ :NS
Ba	Ap	NS	$T_1$ :Ap<Bg	$T_1 < T_2$	$T_1$ :Ap<Bg	$T_1 > T_2$	$T_1$ :NS
	Bg	$T_1 > T_2$	$T_2$ :NS	NS	$T_2$ :NS	NS	$T_2$ :Ap<Bg
Be	Ap	NS	$T_1$ :NS	NS	$T_1$ :NS	NS	$T_1$ :NS
	Bg	NS	$T_2$ :NS	NS	$T_2$ :NS	NS	$T_2$ :NS
Ca	Ap	NS	$T_1$ :Ap<Bg	NS	$T_1$ :Ap<Bg	NS	$T_1$ :Ap<Bg
	Bg	NS	$T_2$ :NS	NS	$T_2$ :Ap<Bg	NS	$T_2$ :Ap<Bg
Co	Ap	NS	$T_1$ :Ap<Bg	$T_1 < T_2$	$T_1$ :NS	NS	$T_1$ :NS
	Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :Ap<Bg
Cr	Ap	NS	$T_1$ :NS	$T_1 < T_2$	$T_1$ :NS	NS	$T_1$ :NS
	Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :NS
Cu	Ap	NS	$T_1$ :NS	$T_1 < T_2$	$T_1$ :NS	NS	$T_1$ :NS
	Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :NS	NS	$T_2$ :Ap>Bg
Fe	Ap	NS	$T_1$ :NS	NS	$T_1$ :Ap<Bg	NS	$T_1$ :NS
	Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :NS
K	Ap	NS	$T_1$ :Ap<Bg	$T_1 < T_2$	$T_1$ :Ap<Bg	NS	$T_1$ :NS
	Bg	$T_1 > T_2$	$T_2$ :NS	NS	$T_2$ :NS	NS	$T_2$ :Ap<Bg
La	Ap	NS	$T_1$ :Ap<Bg	$T_1 < T_2$	$T_1$ :NS	NS	$T_1$ :NS
	Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :NS
Mg	Ap	NS	$T_1$ :NS	NS	$T_1$ :Ap<Bg	NS	$T_1$ :Ap<Bg
	Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :Ap<Bg
Mn	Ap	NS	$T_1$ :Ap<Bg	NS	$T_1$ :Ap<Bg	NS	$T_1$ :Ap<Bg
	Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :Ap<Bg
Na	Ap	NS	$T_1$ :NS	NS	$T_1$ :Ap<Bg	NS	$T_1$ :Ap<Bg
	Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :NS	NS	$T_2$ :Ap<Bg
Ni	Ap	NS	$T_1$ :NS	$T_1 < T_2$	$T_1$ :NS	NS	$T_1$ :NS
	Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :Ap<Bg
P	Ap	NS	$T_1$ :Ap<Bg	NS	$T_1$ :Ap<Bg	NS	$T_1$ :Ap>Bg
	Bg	NS	$T_2$ :Ap<Bg	$T_1 < T_2$	$T_2$ :Ap<Bg	NS	$T_2$ :Ap>Bg
Si	Ap	NS	$T_1$ :NS	NS	$T_1$ :NS	NS	$T_1$ :Ap>Bg
	Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :Ap<Bg	$T_1 < T_2$	$T_2$ :NS
Sr	Ap	$T_1 < T_2$	$T_1$ :NS	NS	$T_1$ :NS	NS	$T_1$ :Ap<Bg
	Bg	NS	$T_2$ :NS	NS	$T_2$ :NS	NS	$T_2$ :Ap<Bg
Ti	Ap	NS	$T_1$ :NS	NS	$T_1$ :NS	NS	$T_1$ :NS
	Bg	NS	$T_2$ :NS	NS	$T_2$ :NS	NS	$T_2$ :Ap>Bg
V	Ap	NS	$T_1$ :Ap<Bg	$T_1 < T_2$	$T_1$ :NS	NS	$T_1$ :NS
	Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :Ap>Bg
Yb	Ap	NS	$T_1$ :Ap<Bg	$T_1 < T_2$	$T_1$ :NS	NS	$T_1$ :NS
	Bg	NS	$T_2$ :Ap<Bg	NS	$T_2$ :NS	NS	$T_2$ :NS
Zn	Ap	NS	$T_1$ :NS	$T_1 < T_2$	$T_1$ :NS	NS	$T_1$ :NS
	Bg	NS	$T_2$ :NS	NS	$T_2$ :Ap<Bg	NS	$T_2$ :NS



Table 13. (cont'd)

- <sup>1</sup> Fractions are from soil samples collected from three locations at 20, 50 and 80 m and 10, 50 and 70 m along the transects in fields 1 and 2, respectively.
- <sup>2</sup> Based on t tests ( $p = 0.05$ ) with typically 4 degrees of freedom. NS: not significantly different. For Sr (Ap, sand), Ba (Ap, silt), Cu (Ap, silt), Ni (Ap, silt), Zn (Ap, silt), Ba (Ap, clay) and K (Bg, sand) the differences are also significant at  $p = 0.01$ .
- <sup>3</sup> Based on t tests ( $p = 0.05$ ) with typically 4 degree of freedom. In field 1 the following differences are significant also at  $p = 0.01$ ; K, La, Mn and Yb in sand; Al, Ca, Mg, Na and P in silt; Ca, Mg, Mn, Na, P and Sr in clay. In field 2 the following differences are significant also at  $p = 0.01$ ; Co, La, Ni, Si and V in sand; Ca, Co, Cr, Fe, Mg, Ni, P, Si, V and Zn in silt; Ba, Co, Cu, K, Mn, Na, Ni, P and Ti in clay.

Table 14. Summary of statistical comparisons of total elemental concentrations in soil fractions of two fields<sup>1</sup>.

Component	Ap Horizon		Bg Horizon	
	T1 < T2	T1 > T2	T1 < T2	T1 > T2
Sand	Sr*	Al	-	Ba, K*
Silt	Ba*, Na	Co, Cr, Cu* K, La, Ni* V, Yb, Zn*	-	P
Clay	-	Ba*, Be*	Si	-

- <sup>1</sup> Based on t tests ( $p = 0.05$ ) with 4 degrees of freedom. For elements marked with an asterisk, concentration differences are also significant at  $p = 0.01$ . Only those elements with significant concentration differences are listed. Elements for which calculations were carried out are: Al, Ba, Be, Ca, Co, Cr, Cu, Fe, K, La, Mg, Mn, Na, Ni, P, Si, Sr, Ti, V, Yb, Zn.

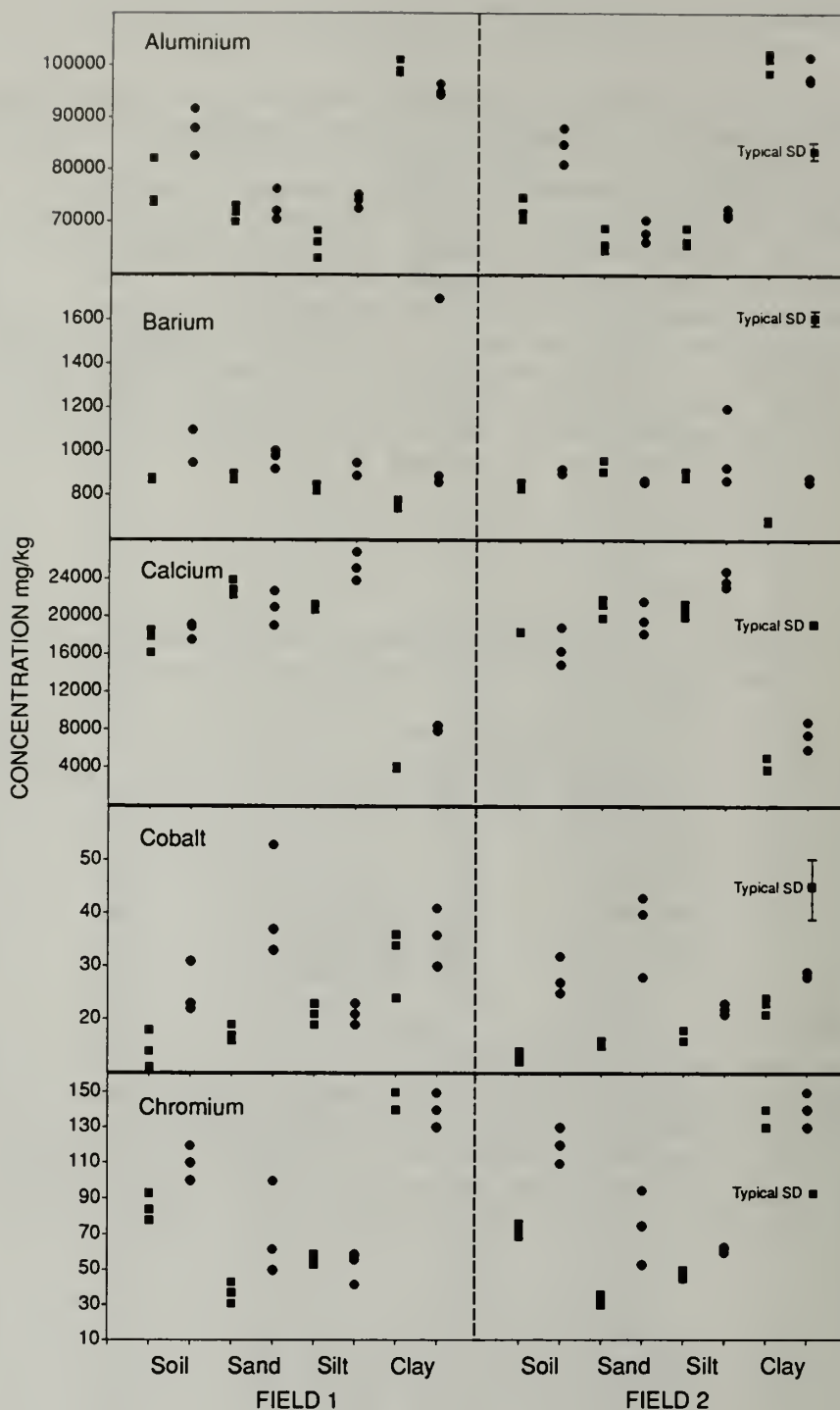


FIGURE 6. Total concentrations (mg/kg) of Al, Ba, Ca, Co and Cr in sand, silt and clay portions in surface (Ap) and subsurface (Bg) horizons from three locations at 20, 50 and 80 m and 10, 50 and 70 m along transects in fields 1 and 2 respectively. Data for whole soil from the corresponding three locations are included for comparison;  $\square$ :Ap,  $\bullet$ :Bg. Typical one standard deviations of individual determinations (analytical precision) are indicated by labelled points at the right of each plot.

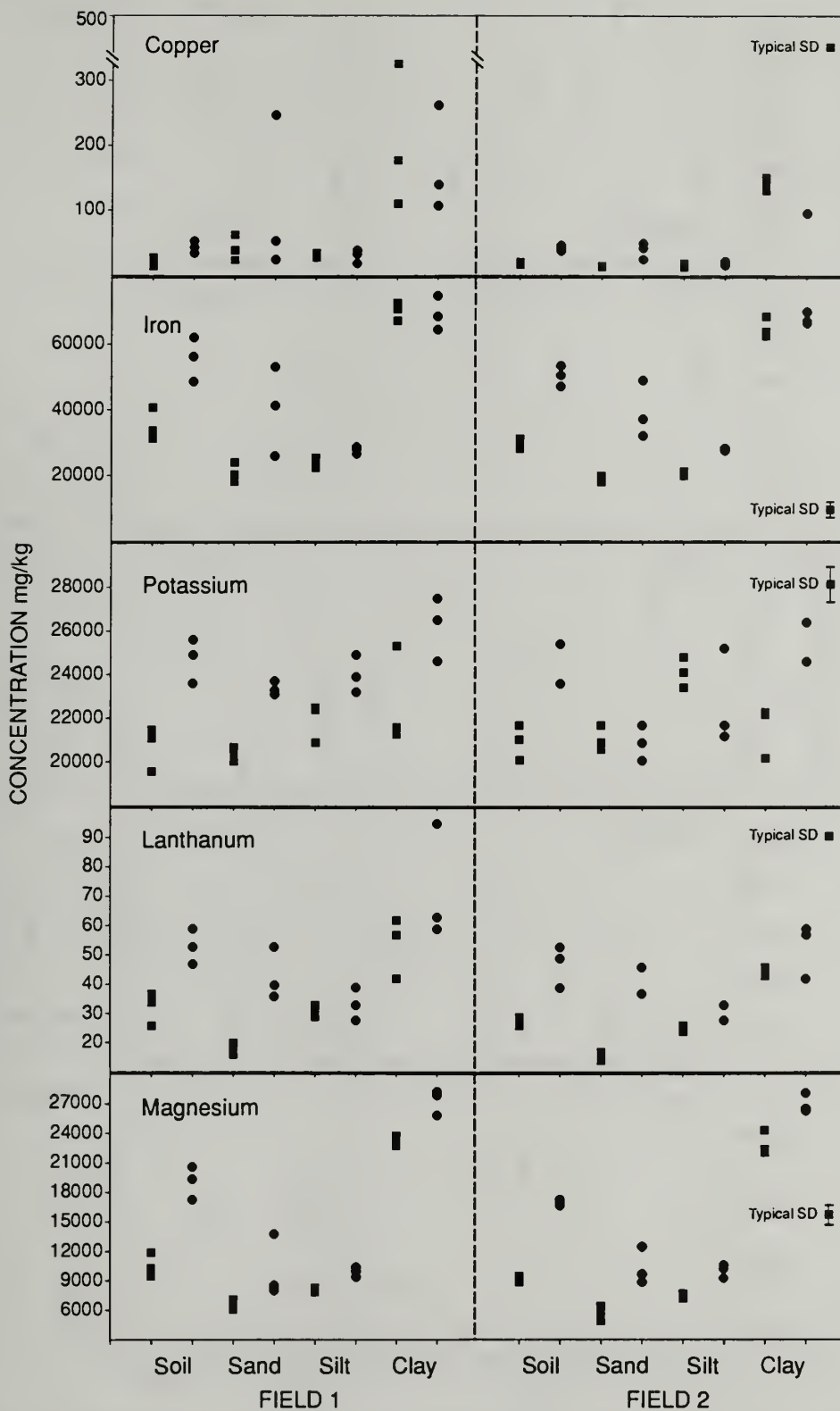


FIGURE 7. Total concentrations (mg/kg) of Cu, Fe, K, La and Mg in sand, silt and clay portions in surface (Ap) and subsurface (Bg) horizons from three locations at 20, 50 and 80 m and 10, 50 and 70 m along transects in fields 1 and 2 respectively. Refer to caption to fig. 6 for details.

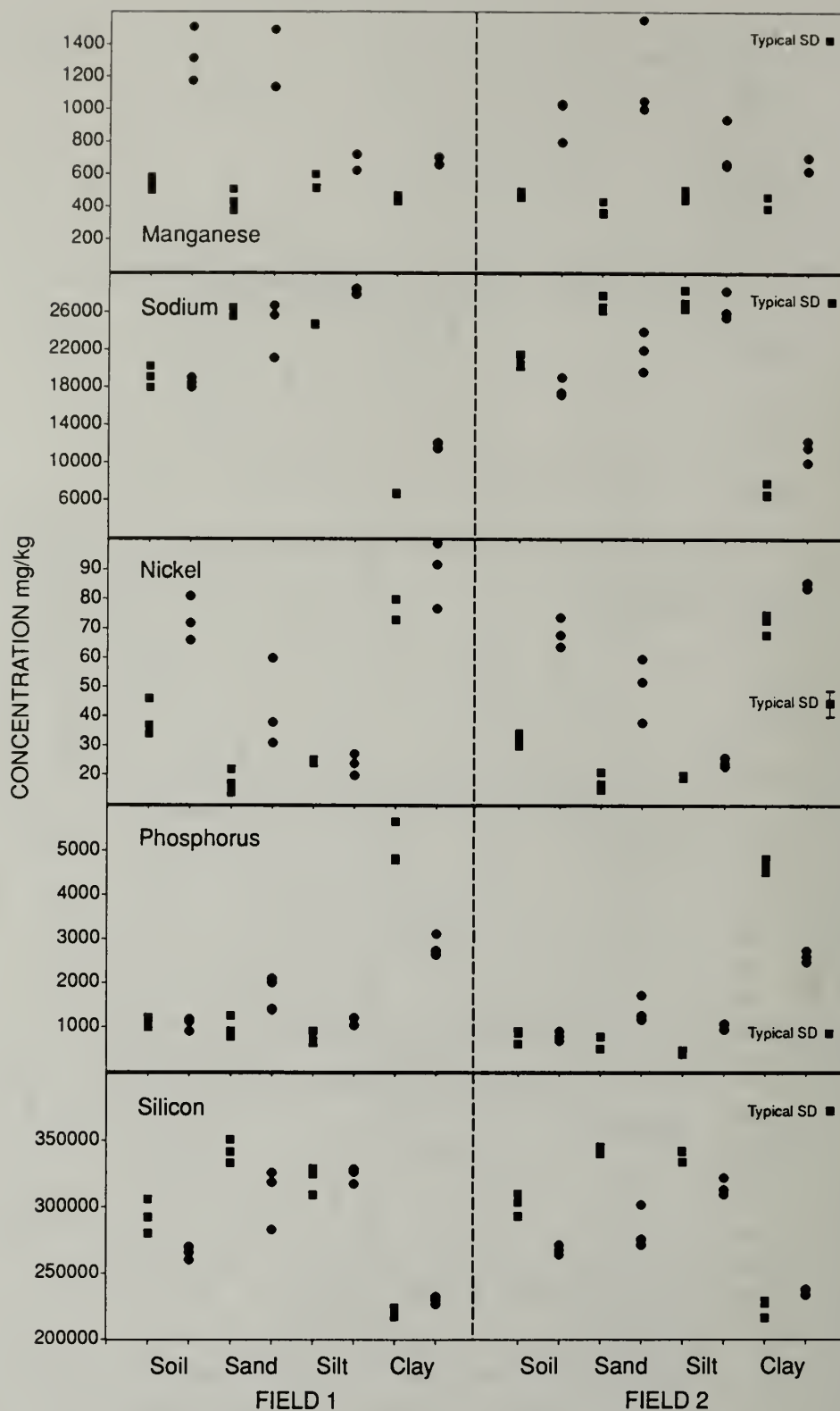


FIGURE 8. Total concentrations (mg/kg) of Mn, Na, Ni, P and Si in sand, silt and clay portions in surface (Ap) and subsurface (Bg) horizons from the three locations at 20, 50 and 80 m and 10, 50 and 70 m along transects in fields 1 and 2 respectively. Refer to caption to fig. 6 for details.



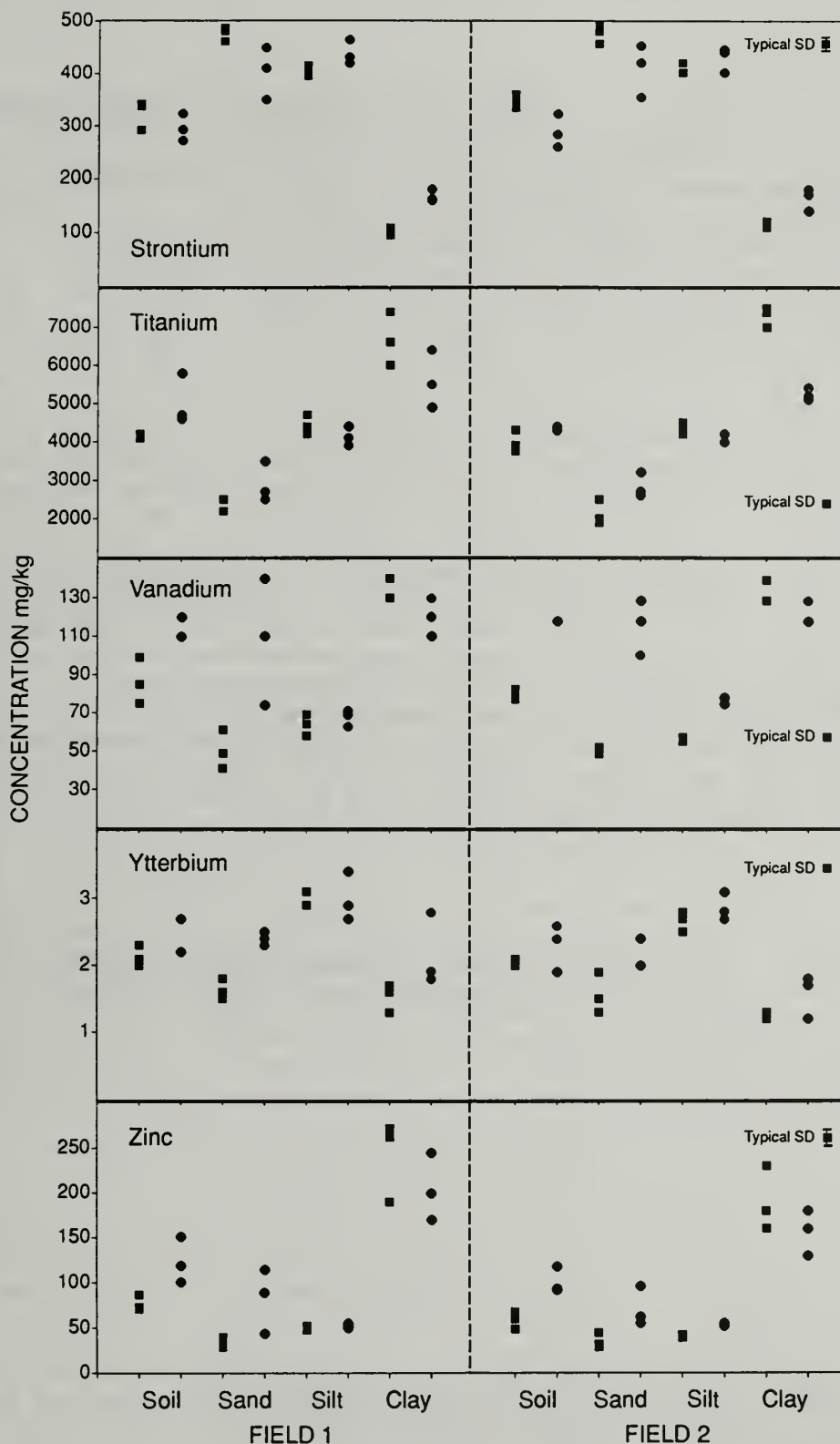


FIGURE 9. Total concentrations (mg/kg) of Sr, Ti, V, Yb and Zn in sand, silt and clay portions in surface (Ap) and subsurface (Bg) horizons from the three locations at 20, 50 and 80 m and 10, 50 and 70 m along transects in fields 1 and 2 respectively. Refer to caption to figure 6 for details.

Table 15. Summary of statistical comparisons of total elemental concentrations in soil fractions in two horizons<sup>1</sup>.

Component	Field 1		Field 2	
	Ap < Bg	Ap > Bg	Ap < Bg	Ap > Bg
Sand	Ba, Be, Co K*, La*, Mn* P, V, Yb*	Ca	Be*, Co*, Cr Cu, Fe, La* Mg, Mn, Na Ni, P, V*, Yb	Si*
Silt	Al*, Ba, Ca Fe, K, Mg* Mn, Na*, P*	-	Al, Ca*, Co* Cr*, Fe*, La Mg*, Mn, Ni* P*, V*, Zn*	P
Clay	Ca*, Mg*, Mn* Na*, Si, Sr*	Al, P*	Ba, Be, Ca Co, K, Mg Mn, Na, Ni, Sr	Cu, P Ti, V

<sup>1</sup> Based on t tests ( $p = 0.05$ ) with 4 degrees of freedom.

\* For elements marked with an asterisk, concentration differences are also significant at  $p = 0.01$ . Only those elements with significant concentration differences are listed. Elements for which calculations were carried out are: Al, Ba, Be, Ca, Co, Cr, Cu, Fe, K, La, Mg, Mn, Na, Ni, P, Si, Sr, Ti, V, Yb, Zn.

Table 16. Comparisons of total elemental concentrations in soil fractions in two horizons (elements common to both fields)<sup>1</sup>.

Component	Ap < Bg	Ap > Bg
Sand	Be, Co, La* Mn, P, Yb	-
Silt	Al, Ca, Fe Mg*, Mn, P*	-
Clay	Ca, Mg, Mn Na, Sr	P

<sup>1</sup> Elements with identical behaviour in both fields. Based on t tests ( $p = 0.05$ ) with 4 degrees of freedom applied individually to data for each field.

\* Elements with an asterisk exhibit highly significant differences ( $p = 0.01$ ) in both field.

## Extractable Elemental Concentrations in Soils

Concentrations of elements determined using partial (as opposed to total dissolution procedures upon which have been based all concentrations discussed up till now) extractive procedures relate to the bioavailable elemental fraction taken up and utilizable by the crop. Thus several essential and toxicologically-pertinent trace elements were determined by those different commonly-used extraction procedures. Basic results including minimum, maximum and mean concentrations, standard deviations and CV's are presented in Tables 17-22 for each field and horizon. The CV's listed there essentially reflect concentration variations with sampling location. Figures 10 and 11 are two typical diagrammatic examples for Cu and Mn, respectively, depicting extractable concentrations as functions of position along the transect for each field; each includes plots of total concentrations for comparison. Several interesting conclusions are evident from visual inspection of these and similar plots.

Firstly, the usual sequence of increasing efficacy of extraction from these soils was DTPA<EDTA<HCl for samples from the Ap horizon and DTPA<EDTA=HCl for those from the Bg horizon. Secondly, the plot patterns for the different extractants quite closely follow each other within the same field and horizon. Finally, there is reasonable concordance between corresponding plots of extractable and total concentrations; that is, occurrences of minima and maxima and trends in the total concentration plots are generally reflected, and even magnified in the extractable plots.

Another way of presenting extractable concentration results is as ratios to total concentrations. Extractable/total elemental concentration ratios are presented in Tables 23-25 for the seven elements, Co, Cr, Cu, Mn, Ni, V and Zn for which total concentrations are also available (total levels of Cd and Pb in soils were not available in this work). For each element, minimum, maximum and mean ratios and standard deviations for each horizon and field are listed. Perusal of this tabulated information indicated that, over all elements, the typical sequence of increasing efficacy of extraction was DTPA<EDTA<HCl for samples from the Ap horizon, in exact agreement with the sequence deduced from concentration data. For samples from the Bg horizon, the sequence was DTPA<HCl<EDTA differing slightly from the DTPA<EDTA=HCl sequence registered for concentration data. A comparison can also be made of efficacy of extraction with respect to the individual elements. For soil samples from the Ap horizon of both fields, the consensus sequence of extraction efficacy over all three extractants is Cr < Zn < Ni < Co < Mn < Cu, whereas for samples from the Bg horizon, the sequence is Cr < Ni < Zn < Cu < Co < Mn. Over all conditions of fields, horizons and extractants, the sequence is Cr < Ni < Zn < Cu < Mn < Co. This means that commonly-used extractive procedures release a smaller portion of the total Cr, Ni ... than of Mn and Co and that the latter elements are estimated to be more readily available for uptake by crops than the former elements.

Results of statistical tests using extractable concentrations are summarized in tables 26-28 for DTPA, EDTA and HCl extractants, respectively. In each table, mean concentrations are compared between fields within the same horizon using t tests ( $p = 0.05$ ) with typically 17 degrees of freedom, mean concentrations are compared between horizons within each field (t test,  $p = 0.05$ , 17-18 degrees of freedom) and variances of mean concentrations are compared

Table 17. DTPA-extractable elemental concentrations (mg/kg) in soils of Field 1<sup>1</sup>.

Element	Horizon	Minimum.	Maximum	Mean	SD	CV(%)
Cd	Ap	0.02	0.06	0.037	0.015	40
	Bg	0.04	0.04	0.04	-	-
Co	Ap	0.04	0.37	0.22	0.11	50
	Bg	0.09	0.63	0.34	0.18	53
Cr	Ap	0.10	0.40	0.22	0.11	50
	Bg	0.10	0.10	0.10	-	-
Cu	Ap	0.77	2.43	1.57	0.45	29
	Bg	1.25	2.45	1.97	0.46	23
Mn	Ap	9.40	30.1	22.3	6.7	30
	Bg	14.7	77.8	36.2	19.7	55
Ni	Ap	0.29	0.82	0.45	0.16	36
	Bg	0.27	0.69	0.45	0.14	32
Pb	Ap	1.17	2.48	2.07	0.48	23
	Bg	0.75	1.54	1.22	0.22	18
V	Ap	-	-	-	-	-
	Bg	-	-	-	-	-
Zn	Ap	0.57	1.25	0.93	0.27	29
	Bg	0.56	5.73	2.21	1.93	87

<sup>1</sup> Based on analyses of 1-10 (typically 10) samples from one 100 m transect.

between the two fields using F tests ( $p = 0.05$ ) with 8/9 or 9/8 degrees of freedom.

For comparisons of means between fields, fourteen out of a total of 47 statistical tests showed significant differences with concentrations in field 1 exceeding those in field 2 in 11 instances. The elements Mn and Zn were the dominant ones exhibiting differences. About 3/4 of tests of means between horizons showed significant behaviour involving all elements, with concentrations in the Ap horizon being greater than those in the Bg horizon in all significant DTPA comparisons, and generally the opposite behaviour with EDTA and HCl. A comparison of variances of mean extractable concentrations indicated only 1/5th of the tests to be significantly different, with variations among locations in field 1 invariably greater than those in field 2.



Table 18. EDTA-extractable elemental concentrations (mg/kg) in soils of Field 1<sup>1</sup>.

Element	Horizon	Minimum	Maximum	Mean	SD	CV(%)
Cd	Ap	0.12	0.16	0.14	0.016	11
	Bg	0.08	0.15	0.11	0.021	19
Co	Ap	0.31	1.68	0.74	0.38	52
	Bg	1.29	6.52	3.64	1.63	45
Cr	Ap	0.10	0.66	0.30	0.18	59
	Bg	0.31	1.12	0.64	0.26	42
Cu	Ap	1.11	3.07	2.03	0.53	26
	Bg	1.68	3.83	2.96	0.78	26
Mn	Ap	12.3	78.23	5.3	18.1	51
	Bg	114	495	256	133	52
Ni	Ap	0.76	1.66	1.07	0.28	26
	Bg	0.92	4.15	2.32	0.96	41
Pb	Ap	0.29	3.38	2.58	0.95	37
	Bg	0.34	1.62	1.22	0.38	34
V	Ap	1.02	2.55	1.56	0.41	26
	Bg	1.68	4.03	2.42	0.63	26
Zn	Ap	1.03	2.97	1.90	0.48	28
	Bg	0.97	5.12	3.12	1.42	46

<sup>1</sup> Based on analyses of 10 samples from one 100 m transect.

Statistical behaviour of extractable elemental concentrations documented in Tables 26-28 was compared with the statistical behaviour for total elemental concentrations reported previously in Table 7. Comparisons were made of the corresponding treatments (means between fields, means between horizons and variances between fields) to check for similarities or differences between these two measures of trace element content for common elements. Generally there was good agreement, with better agreement for both the EDTA and HCl results. Concordance of the DTPA statistical results with total concentration data was less evident with a glaring total lack of agreement between means between horizons.

Table 19. HCl-extractable elemental concentrations (mg/kg) in soils of Field 1<sup>1</sup>.

Element	Horizon	Minimum	Maximum	Mean	SD	CV(%)
Cd	Ap	0.06	0.21	0.12	0.048	40
	Bg	0.07	0.16	0.12	0.033	28
Co	Ap	0.45	2.28	1.37	0.55	40
	Bg	1.20	2.80	2.13	0.47	22
Cr	Ap	0.80	2.70	1.83	0.58	32
	Bg	2.00	2.90	2.50	0.34	14
Cu	Ap	1.04	1.98	1.33	0.37	28
	Bg	1.07	3.20	2.13	0.61	29
Mn	Ap	12.9	94.9	52.4	22.1	42
	Bg	81	166.0	115.0	30.0	26
Ni	Ap	0.54	2.09	0.93	0.47	51
	Bg	0.82	2.45	1.83	0.58	32
Pb	Ap	-	-	-	-	-
	Bg	-	-	-	-	-
V	Ap	1.30	3.60	2.48	0.88	36
	bg	0.40	3.50	1.61	1.02	64
Zn	Ap	1.41	4.68	2.39	1.17	49
	Bg	2.26	7.09	4.99	1.24	25

1 Based on analyses of 7-10 (typically 10) samples from one 100 m transect.

Regression correlation calculations using the individual concentration data were carried out among the different extractable concentrations (DTPA-EDTA, DTPA-HCl, EDTA-HCl) and between extractable and total concentrations (DTPA-total, EDTA-total, HCl-total). Correlations are summarized for surface Ap and subsurface Bg horizons for both fields in Tables 29 and 30 respectively. For the Ap horizon, out of a total of 84 correlations among all six possible extractable-extractable and extractable-total concentrations, 42 or one-half are significant. Similarly, for correlations of Bg results, 31 out of 84 or less than one-half are significant. Generally, the majority of significant correlations are also highly significant ( $p = 0.01$ ) and are similar in both fields. Elements most prominent are Mn, Co, Cu and Ni.

Table 20. DTPA-extractable elemental concentrations (mg/kg) in soils of Field 2<sup>1</sup>.

Element	Horizon	Minimum	Maximum	Mean	SD	CV(%)
Cd	Ap	0.01	0.05	0.03	0.02	70
	Bg	0.24	0.24	0.24	-	-
Co	Ap	0.09	0.32	0.20	0.078	38
	Bg	0.17	0.38	0.26	0.064	25
Cr	Ap	0.10	0.30	0.20	0.064	25
	Bg	0.10	0.10	0.10	-	-
Cu	Ap	0.81	1.72	1.20	0.35	29
	Bg	0.89	1.94	1.58	0.30	19
Mn	Ap	7.0	18.8	11.5	4.2	37
	Bg	16.1	26.1	18.8	2.9	16
Ni	Ap	0.32	0.85	0.52	0.15	29
	Bg	0.27	0.45	0.36	0.06	17
Pb	Ap	1.54	3.27	2.44	0.57	23
	Bg	0.54	1.38	1.05	0.24	23
V	Ap	-	-	-	-	-
	Bg	-	-	-	-	-
Zn	Ap	0.55	1.44	0.90	0.35	39
	Bg	0.48	1.44	0.76	0.33	43

<sup>1</sup> Based on analyses of 1-10 (typically 9) samples from one 100 m transect.

Table 21. EDTA-extractable elemental concentrations (mg/kg) in soils of Field 2<sup>1</sup>.

Element	Horizon	Minimum	Maximum	Mean	SD	CV(%)
Cd	Ap	0.12	0.16	0.13	0.012	9.2
	Bg	0.02	0.09	0.07	0.02	28
Co	Ap	0.63	1.97	1.12	0.47	42
	Bg	3.01	4.88	3.70	0.70	19
Cr	Ap	0.46	1.22	0.89	0.25	29
	Bg	0.46	1.43	0.88	0.26	29
Cu	Ap	1.21	2.63	1.96	0.57	29
	Bg	1.65	3.08	2.46	0.43	17
Mn	Ap	20.0	64.1	36.9	15.8	43
	Bg	103.0	229.0	148.0	35.0	24
Ni	Ap	0.60	1.98	1.13	0.42	37
	Bg	1.28	3.23	1.79	0.59	33
Pb	Ap	2.32	3.99	2.90	0.51	18
	Bg	0.92	1.58	1.17	0.21	18
V	Ap	1.07	2.04	1.51	0.31	20
	Bg	1.43	3.11	2.18	0.52	24
Zn	Ap	0.97	2.08	1.23	0.42	34
	Bg	0.80	2.08	1.07	0.36	34

<sup>1</sup> Based on analyses of 9-10 (typically 9) samples from one 100 m transect.



Table 22. HCl-extractable elemental concentrations (mg/kg) in soils of Field 2<sup>1</sup>.

Element	Horizon	Minimum	Maximum	Mean	SD	CV(%)
Cd	Ap	0.06	0.15	0.10	0.034	34
	Bg	0.03	0.03	0.03	-	-
Co	Ap	1.01	2.20	1.46	0.41	28
	Bg	2.80	4.18	3.31	0.43	13
Cr	Ap	0.90	2.70	1.88	0.74	39
	Bg	1.90	2.80	2.38	0.31	13
Cu	Ap	1.18	2.10	1.43	0.32	22
	Bg	2.07	2.57	2.23	0.16	7.2
Mn	Ap	34.5	64.7	47.1	9.9	21
	Bg	81.4	148	111	18.6	17
Ni	Ap	1.05	1.95	1.41	0.30	21
	Bg	1.05	2.86	1.74	0.58	33
Pb	Ap	-	-	-	-	-
	Bg	-	-	-	-	-
V	Ap	0.60	2.30	1.67	0.61	37
	Bg	1.20	4.70	2.52	1.22	48
Zn	Ap	0.60	2.11	1.45	0.65	45
	Bg	1.63	5.32	2.96	1.42	48

<sup>1</sup> Based on analyses of 1-10 (typically 9) samples from one 100 m transect.

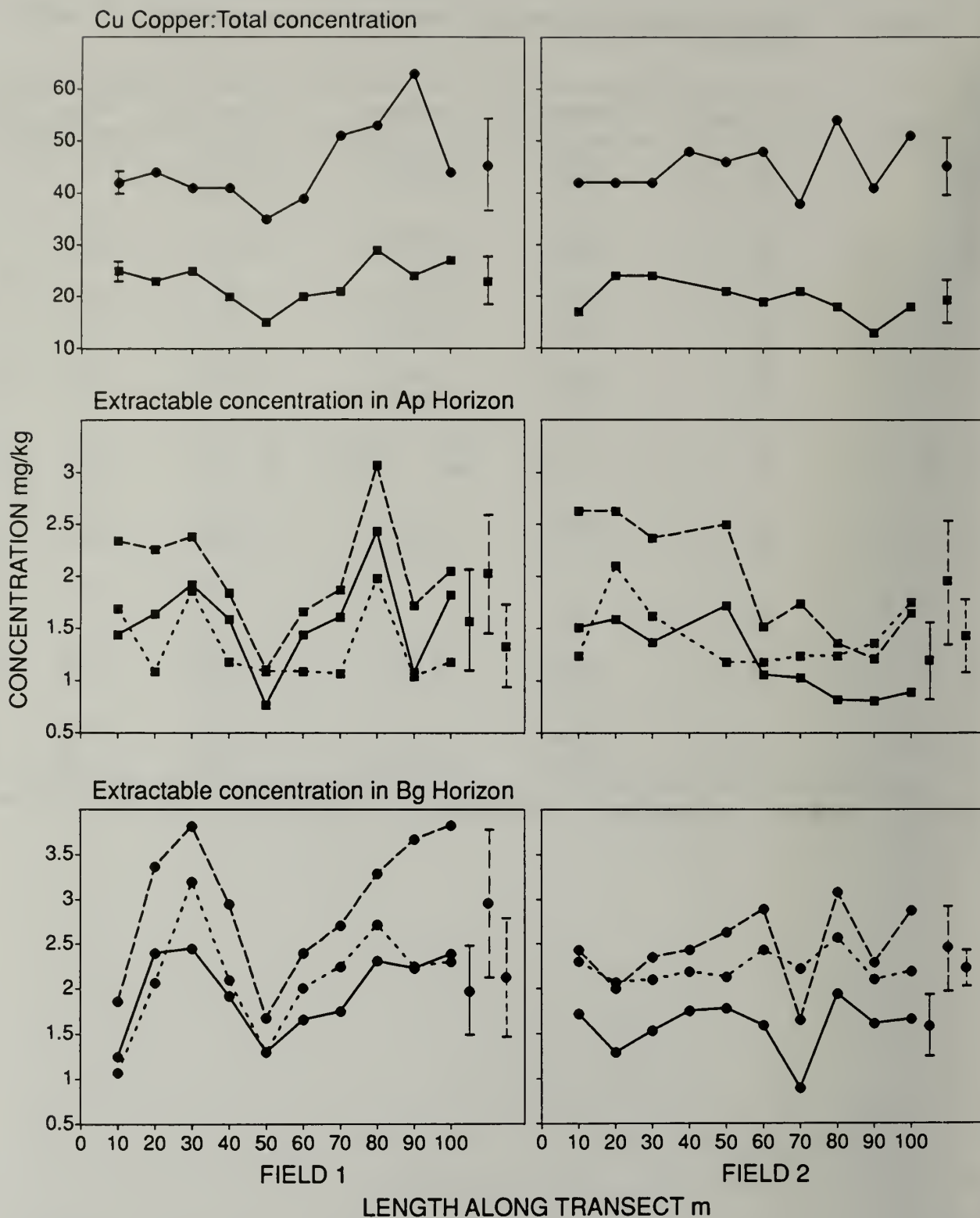
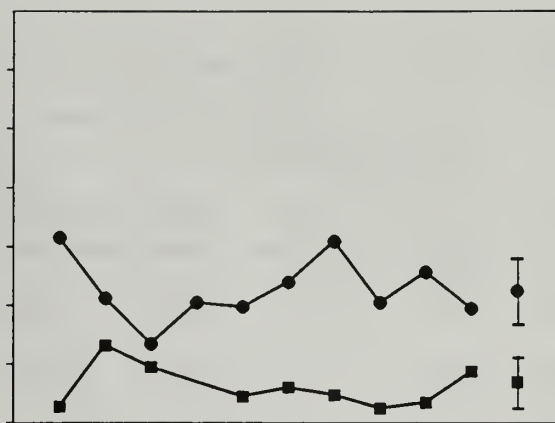
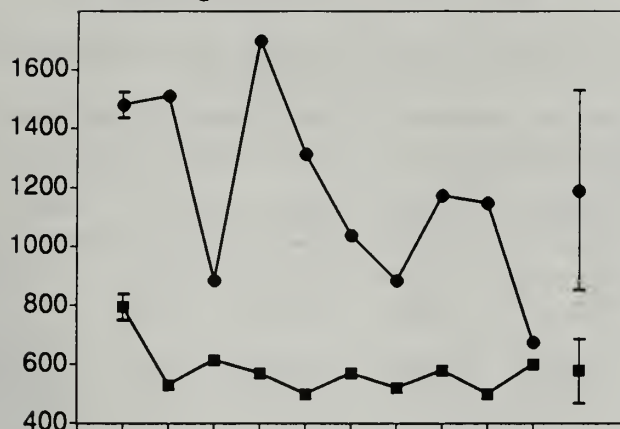
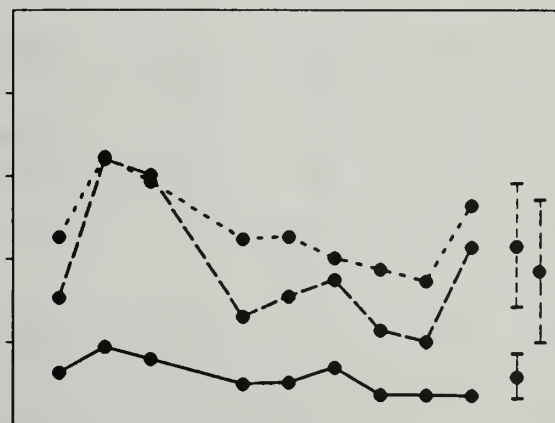
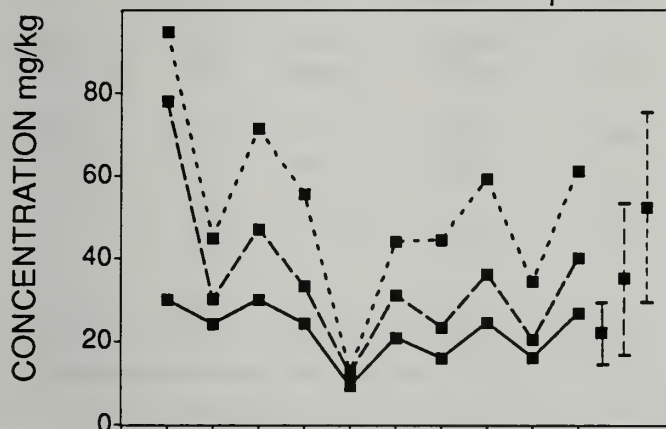


FIGURE 10. Extractable concentrations of copper measured by extraction with DTPA (—), EDTA (---) and HCl (····) in surface (Ap) and subsurface (Bg) horizons along one transect in each of the two fields. The points at the right of each compartment are means  $\pm$  one standard deviation. Plots of total concentrations are included for comparison;  $\square$ :Ap,  $\bullet$ :Bg horizons.

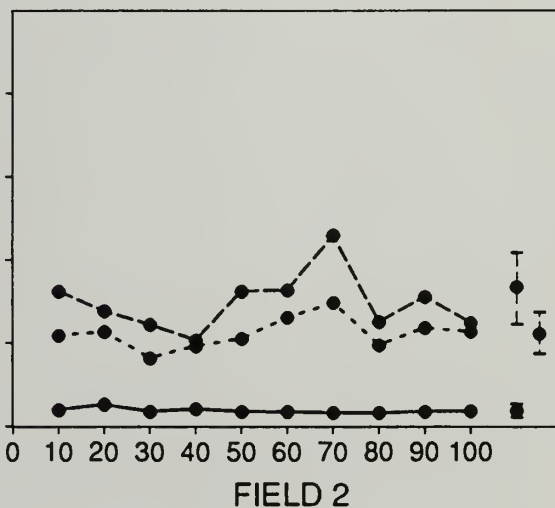
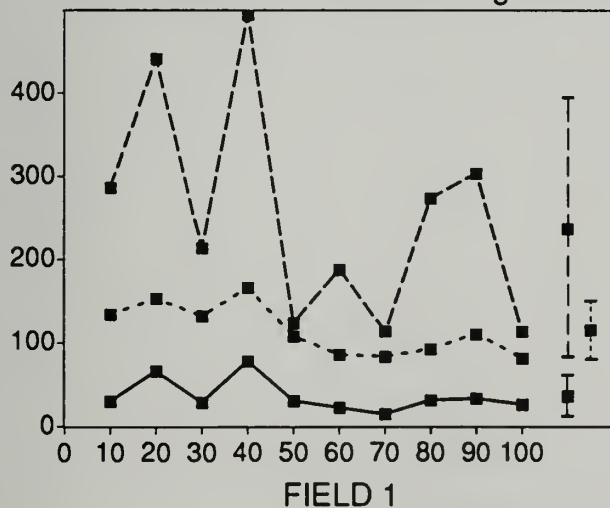
# Mn Manganese: Total Concentration



## Extractable concentration in Ap Horizon



## Extractable concentration in Bg Horizon



LENGTH ALONG TRANSECT m

FIGURE 11. Extractable concentrations of manganese measured by extraction with DTPA (—), EDTA (---) and HCl (- - -) in surface (Ap) and subsurface (Bg) horizons along one transect in each of the two fields. The points at the right of each compartment are means  $\pm$  one standard deviation. Plots of total concentrations are included for comparison;  $\square$ : Ap,  $\bullet$ : Bg horizons.

Table 23. DTPA-extractable/total elemental concentration ratios for soils from the two fields.

Element	Horizon	Extractable/total concentration ratio <sup>1</sup>							
		Field 1				Field 2			
		Min.	Max.	Mean	SD	Min.	Max.	Mean	SD
Co	Ap	0.0031	0.0225	0.0144	0.0066	0.0080	0.020	0.015	0.005
	Bg	0.0027	0.0210	0.0123	0.0061	0.0057	0.015	0.012	0.002
Cr	Ap	0.0011	0.0051	0.0026	0.0014	0.0014	0.0039	0.0029	0.0010
	Bg	-	-	0.00083	-	-	-	0.0008	-
Cu	Ap	0.0450	0.0838	0.0681	0.0128	0.046	0.089	0.062	0.015
	Bg	0.030	0.060	0.044	0.010	0.023	0.041	0.035	0.005
Mn	Ap	0.0188	0.0489	0.0382	0.0089	0.012	0.028	0.022	0.006
	Bg	0.017	0.046	0.030	0.010	0.016	0.032	0.022	0.005
Ni	Ap	0.0074	0.0182	0.0108	0.0034	0.012	0.024	0.016	0.004
	Bg	0.0034	0.0090	0.0062	0.0018	0.0036	0.0061	0.0051	0.0008
V	Ap	-	-	-	-	-	-	-	-
	Bg	-	-	-	-	-	-	-	-
Zn	Ap	0.00648	0.0172	0.0112	0.0036	0.0095	0.029	0.016	0.006
	Bg	0.0059	0.039	0.017	0.013	0.0052	0.0126	0.0074	0.0028

<sup>1</sup> Ratio of extractable concentration to total concentration in soil samples from typically 10 locations from one transect in each field.



Table 24. EDTA-extractable/total elemental concentration ratios for soils from the two fields.

Element	Horizon	Extractable/total concentration ratio <sup>1</sup>							
		Field 1				Field 2			
		Min.	Max.	Mean	SD	Min.	Max.	Mean	SD
Co	Ap	0.025	0.080	0.047	0.017	0.061	0.121	0.081	0.018
	Bg	0.080	0.192	0.135	0.047	0.105	0.169	0.145	0.022
Cr	Ap	0.0011	0.0069	0.0033	0.0018	0.0074	0.036	0.0016	0.009
	Bg	0.0026	0.0086	0.0053	0.0020	0.0042	0.012	0.0075	0.0022
Cu	Ap	0.072	0.106	0.088	0.011	0.076	0.155	0.101	0.025
	Bg	0.044	0.093	0.066	0.016	0.043	0.060	0.054	0.005
Mn	Ap	0.025	0.098	0.059	0.020	0.043	0.102	0.069	0.020
	Bg	0.094	0.293	0.209	0.067	0.127	0.225	0.173	0.028
Ni	Ap	0.017	0.037	0.026	0.006	0.022	0.057	0.036	0.011
	Bg	0.014	0.043	0.032	0.012	0.017	0.050	0.026	0.010
V	Ap	0.012	0.034	0.018	0.006	0.0143	0.025	0.021	0.004
	Bg	0.0153	0.034	0.021	0.005	0.013	0.028	0.020	0.005
Zn	Ap	0.012	0.042	0.023	0.007	0.016	0.031	0.021	0.005
	Bg	0.009	0.037	0.025	0.009	0.0086	0.018	0.011	0.003

<sup>1</sup> Ratio of extractable concentration to total concentration in soil samples from typically 10 locations from one transect in each field.

Table 25. HCl-extractable/total elemental concentration ratios for soils from the two fields.

Element	Horizon	Extractable/total concentration ratio <sup>1</sup>							
		Field 1				Field 2			
		Min.	Max.	Mean	SD	Min.	Max.	Mean	SD
Co	Ap	0.041	0.134	0.088	0.027	0.086	0.147	0.108	0.019
	Bg	0.054	0.144	0.083	0.024	0.093	0.161	0.131	0.019
Cr	Ap	0.010	0.029	0.020	0.006	0.013	0.035	0.026	0.009
	Bg	0.014	0.029	0.021	0.005	0.016	0.026	0.020	0.003
Cu	Ap	0.043	0.074	0.058	0.012	0.056	0.105	0.075	0.017
	Bg	0.026	0.078	0.047	0.014	0.043	0.058	0.050	0.004
Mn	Ap	0.026	0.119	0.088	0.027	0.073	0.100	0.089	0.009
	Bg	0.079	0.149	0.099	0.021	0.106	0.148	0.131	0.014
Ni	Ap	0.012	0.046	0.022	0.010	0.033	0.054	0.045	0.007
	Bg	0.013	0.045	0.026	0.009	0.015	0.045	0.025	0.010
V	Ap	0.017	0.040	0.025	0.013	0.009	0.029	0.022	0.007
	Bg	0.003	0.019	0.014	0.008	0.011	0.043	0.023	0.011
Zn	Ap	0.016	0.049	0.028	0.012	0.010	0.034	0.024	0.010
	Bg	0.022	0.059	0.042	0.009	0.018	0.060	0.029	0.014

<sup>1</sup> Ratio of extractable concentration to total concentration in soil samples from typically 10 locations from one transect in each field.

Table 26. Statistical comparisons of DTPA-extractable elemental concentrations

Element	Horizon	Comparison of		
		Means	Variances	Means
		Between fields <sup>1</sup>	Between fields <sup>2</sup>	Between horizons <sup>3</sup>
Cd	Ap	NS	NS	T <sub>1</sub> : -
	Bg	-	-	T <sub>2</sub> : -
Co	Ap	NS	NS	T <sub>1</sub> : NS
	Bg	NS	T <sub>1</sub> > T <sub>2</sub>	T <sub>2</sub> : NS
Cr	Ap	NS	NS	T <sub>1</sub> : -
	Bg	-	-	T <sub>2</sub> : -
Cu	Ap	NS	NS	T <sub>1</sub> : NS
	Bg	T <sub>1</sub> > T <sub>2</sub>	NS	T <sub>2</sub> : Ap > Bg
Mn	Ap	T <sub>1</sub> > T <sub>2</sub>	NS	T <sub>1</sub> : Ap > Bg
	Bg	T <sub>1</sub> > T <sub>2</sub>	T <sub>1</sub> > T <sub>2</sub>	T <sub>2</sub> : Ap > Bg
Ni	Ap	NS	NS	T <sub>1</sub> : NS
	Bg	NS	T <sub>1</sub> > T <sub>2</sub>	T <sub>2</sub> : Ap > Bg
Pb	Ap	NS	NS	T <sub>1</sub> : Ap > Bg
	Bg	NS	NS	T <sub>2</sub> : Ap > Bg
V	Ap	-	-	T <sub>1</sub> : -
	Bg	-	-	T <sub>2</sub> : -
Zn	Ap	NS	NS	T <sub>1</sub> : NS
	Bg	T <sub>1</sub> > T <sub>2</sub>	T <sub>1</sub> > T <sub>2</sub>	T <sub>2</sub> : NS

<sup>1</sup> Based on t tests (p = 0.05) with typically 17 degrees of freedom. NS: not significantly different. For Mn in Ap the difference is significant also at p = 0.01.

<sup>2</sup> Based on F tests (p = 0.05) with typically 8/9 or 9/8 degrees of freedom. The following are also significantly different at p = 0.01: Co, Mn and Zn in the Bg horizon.

<sup>3</sup> Based on t tests (p = 0.05) with typically 17-18 degrees of freedom. Pb(T<sub>1</sub>), Mn, Ni and Pb in T<sub>2</sub> are also significantly different at p = 0.01.

Table 27. Statistical comparisons of EDTA-extractable elemental concentrations

Element	Horizon	Comparison of		
		Means	Variances	Means
		Between fields <sup>1</sup>	Between fields <sup>2</sup>	Between horizons <sup>3</sup>
Cd	Ap	NS	NS	T <sub>1</sub> : Ap > Bg
	Bg	T <sub>1</sub> > T <sub>2</sub>	NS	T <sub>2</sub> : Ap > Bg
Co	Ap	NS	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	T <sub>1</sub> > T <sub>2</sub>	T <sub>2</sub> : Ap < Bg
Cr	Ap	T <sub>1</sub> < T <sub>2</sub>	NS	T <sub>1</sub> : Ap < Bg
	Bg	T <sub>1</sub> < T <sub>2</sub>	NS	T <sub>2</sub> : NS
Cu	Ap	NS	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : Ap < Bg
Mn	Ap	NS	NS	T <sub>1</sub> : Ap < Bg
	Bg	T <sub>1</sub> > T <sub>2</sub>	T <sub>1</sub> > T <sub>2</sub>	T <sub>2</sub> : Ap < Bg
Ni	Ap	NS	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : Ap < Bg
Pb	Ap	NS	NS	T <sub>1</sub> : Ap > Bg
	Bg	NS	NS	T <sub>2</sub> : Ap > Bg
V	Ap	NS	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : Ap < Bg
Zn	Ap	T <sub>1</sub> > T <sub>2</sub>	NS	T <sub>1</sub> : Ap < Bg
	Bg	T <sub>1</sub> > T <sub>2</sub>	T <sub>1</sub> > T <sub>2</sub>	T <sub>2</sub> : NS

<sup>1</sup> Based on t tests ( $p = 0.05$ ) with typically 17 degrees of freedom. NS: not significantly different. For Cr (Ap), Zn (Ap), Cd (Bg) and Zn (Bg) the differences are significant also at  $p = 0.01$ .

<sup>2</sup> Based on F tests ( $p = 0.05$ ) with typically 8/9 or 9/8 degrees of freedom. For Mn (Bg) and Zn (Bg) the differences are significant also at  $p = 0.01$ .

<sup>3</sup> Based on t tests ( $p = 0.05$ ) with typically 17-18 degrees of freedom. With the exception of Zn (T<sub>1</sub>), Cu (T<sub>2</sub>) and Ni (T<sub>2</sub>) all means significantly different at  $p = 0.05$  are also significantly different at  $p = 0.01$ .

Table 28. Statistical Comparisons of HCl-extractable Elemental Concentrations

Element	Horizon	Comparison of		
		Means Between fields <sup>1</sup>	Variances Between fields <sup>2</sup>	Means Between horizons <sup>3</sup>
Cd	Ap	NS	NS	T <sub>1</sub> : NS
	Bg	-	NS	T <sub>2</sub> : -
Co	Ap	NS	NS	T <sub>1</sub> : Ap < Bg
	Bg	T <sub>1</sub> < T <sub>2</sub>	NS	T <sub>2</sub> : Ap < Bg
Cr	Ap	NS	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : NS
Cu	Ap	NS	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	T <sub>1</sub> > T <sub>2</sub>	T <sub>2</sub> : Ap < Bg
Mn	Ap	NS	T <sub>1</sub> > T <sub>2</sub>	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : Ap < Bg
Ni	Ap	T <sub>1</sub> < T <sub>2</sub>	NS	T <sub>1</sub> : Ap < Bg
	Bg	NS	NS	T <sub>2</sub> : NS
Pb	Ap	-	-	T <sub>1</sub> : -
	Bg	-	-	T <sub>2</sub> : -
V	Ap	T <sub>1</sub> > T <sub>2</sub>	NS	T <sub>1</sub> : NS
	Bg	NS	NS	T <sub>2</sub> : NS
Zn	Ap	NS	NS	T <sub>1</sub> : Ap < Bg
	Bg	T <sub>1</sub> > T <sub>2</sub>	NS	T <sub>2</sub> : Ap < Bg

<sup>1</sup> Based on t tests ( $p = 0.05$ ) with typically 17 degrees of freedom. NS: not significantly different. For Co (Bg) and Zn (Bg) the differences are significant also at  $p = 0.01$ .

<sup>2</sup> Based on F tests ( $p = 0.05$ ) with typically 8/9 or 9/8 degrees of freedom. For Cu (Bg) the differences are significant also at  $p = 0.01$ .

<sup>3</sup> Based on t tests ( $p = 0.05$ ) with typically 17-18 degrees of freedom. With the exception of Zn (T<sub>2</sub>), all means significantly different at  $p = 0.05$  are also significantly different at  $p = 0.01$ .



Table 29. Correlations of extractable elemental concentrations in surface (Ap) horizons of soils from fields 1 and 2'

Element and Extractant		Total Concentration		DTPA Extractable		EDTA Extractable	
		1	2	1	2	1	2
Cd	DTPA	-	-	-	-	-	-
	EDTA	-	-	-	-	-	-
	HCl	-	-	-	-	*	NS
Co	DTPA	*	NS	-	-	-	-
	EDTA	*	**	NS	NS	-	-
	HCl	*	*	NS	*	**	**
Cr	DTPA	*	NS	-	-	-	-
	EDTA	NS	NS	-	-	-	-
	HCl	*	*	-	-	NS	NS
Cu	DTPA	**	NS	-	-	-	-
	EDTA	**	NS	**	**	-	-
	HCl	*	NS	*	NS	NS	NS
Mn	DTPA	*	**	-	-	-	-
	EDTA	**	**	**	**	-	-
	HCl	**	**	**	**	**	**
Ni	DTPA	NS	NS	-	-	-	-
	EDTA	NS	*	**	**	-	-
	HCl	NS	*	**	NS	**	*
Pb	DTPA	-	-	-	-	-	-
	EDTA	-	-	**	*	-	-
	HCl	-	-	NS	NS	NS	NS
V	DTPA	NS	NS	-	-	-	-
	EDTA	NS	NS	NS	NS	-	-
	HCl	NS	**	NS	NS	-	-
Zn	DTPA	NS	NS	-	-	-	-
	EDTA	NS	**	*	NS	-	-
	HCl	NS	NS	NS	NS	NS	NS

<sup>1</sup> Significant correlations are indicated at  $p = 0.05$  (\*) and  $p = 0.01$  (\*\*). -: No analytical data available correlation not done between identical parameters or repeat correlations omitted; NS: no significant correlation.

Table 30. Correlations of extractable elemental concentrations in subsurface (Bg) horizons of soils from fields 1 and 2.

Element and Extractant		Total Concentration		DTPA Extractable		EDTA Extractable	
		1	2	1	2	1	2
Cd	DTPA	-	-	-	-	-	-
	EDTA	-	-	-	-	-	-
	HCl	-	-	-	-	NS	NS
Co	DTPA	NS	NS	-	-	-	-
	EDTA	*	NS	*	NS	-	-
	HCl	NS	NS	NS	NS	NS	*
Cr	DTPA	NS	NS	-	-	-	-
	EDTA	NS	NS	-	-	-	-
	HCl	NS	NS	-	-	NS	NS
Cu	DTPA	NS	*	-	-	-	-
	EDTA	NS	**	**	**	-	-
	HCl	NS	NS	**	NS	**	NS
Mn	DTPA	**	NS	-	-	-	-
	EDTA	**	**	**	NS	-	-
	HCl	**	**	**	NS	**	**
Ni	DTPA	NS	NS	-	-	-	-
	EDTA	NS	NS	*	NS	-	-
	HCl	NS	NS	*	NS	**	**
Pb	DTPA	-	-	-	-	-	-
	EDTA	-	-	*	NS	-	-
	HCl	-	-	NS	NS	NS	NS
V	DTPA	NS	NS	-	-	-	-
	EDTA	NS	NS	-	-	-	-
	HCl	NS	NS	-	-	NS	NS
Zn	DTPA	**	NS	-	-	-	-
	EDTA	**	*	**	**	-	-
	HCl	*	NS	*	NS	**	NS

<sup>1</sup> Significant correlations are indicated at  $p = 0.05$  (\*) and  $p = 0.01$  (\*\*).  
 -: No analytical data available, correlation not done between identical parameters or repeat correlations omitted; NS: no significant correlation.

## Mineralogical Characterization of Soil

Silt and clay fractions were examined mineralogically. Mineralogical compositions are summarized semiquantitatively in Table 31 listing contents of the nine minerals smectite, vermiculite, chlorite, mica, kaolinite, amphiboles, quartz, microcline, and plagioclase as well as X-ray amorphous material and interstratified mineral indicated by long and intermediate spacings. Samples examined represent three locations along transects in each field and all results in the table are based on average estimates of three independent determinations.

Conclusions drawn from this data are as follows. Mineral associations of the soils from the two fields are similar and differences between the Ap and Bg horizons are small. In the silt fractions, major components are quartz, microcline and plagioclase, a moderate component is X-ray amorphous material and minor-trace components are phyllosilicates such as mica, kaolinite, chlorite, vermiculite, smectite and interstratified mineral. In the clay fractions, the dominant component was X-ray amorphous material, and minor components are the phyllosilicates stated above plus quartz, microcline, plagioclase and amphiboles.

Table 31. Mineralogical characterization of silt and clay fractions from soils of the two fields<sup>1</sup>.

Mineral or phase	Content <sup>2</sup>							
	Field 1				Field 2			
	Silt		Clay		Silt		Clay	
	Ap	Bg	Ap	Bg	Ap	Bg	Ap	Bg
Interstratified mineral (long spacing)	0	tr	tr	tr	tr	*	*	*
Smectite	0	tr	tr	tr	0	tr	0	tr
Vermiculite	tr	tr	*	*	tr	*	*	*
Chlorite	0	0	*	*	0	0	*	*
Mica	tr	*	*	*	tr	tr	*	*
Kaolinite	tr	tr	0	0	0	0	0	0
Amphiboles	*	*	*	*	*	*	*	*
Quartz	**	**	*	*	***	***	*	*
Microcline	***	**	*	*	***	***	*	*
Plagioclase	***	**	*	*	***	**	*	*
X-ray amorphous <sup>3</sup>	**	**	****	****	tr	*	****	***

<sup>1</sup> Fractions from soils collected from three locations at 20, 50 and 80 m and 10, 50 and 70 m along the transects in fields 1 and 2 respectively.

<sup>2</sup> \*\*\*\* dominant, \*\*\* major, \*\* moderate, \* minor, tr trace, 0 none, based on average estimates of the three independent determinations.

<sup>3</sup> Content estimated as 100% - all 10 crystalline minerals detected, by assigning the following percentages: tr (<1%), \* (1-10%), \*\* (10-25%), \*\*\* (25-40%) and \*\*\*\* (>40%).

## Elemental Concentrations and Variability in Crops

Complete tabulations of elemental concentrations determined in the dry corn and alfalfa tissues are presented in Tables 32 and 33. In each table, listed are minimum and maximum contents for each tissues, corn leaves, corn stalk and whole alfalfa observed over the 10 sampling locations along each transect, and means  $\pm$  one standard deviation for 15 elements, 14 in common with the soil measurements, and one, S, in addition only in crops.

Comparison of analytical precisions (SD's for crop tissues listed in Table 1) with SD's in Tables 32 and 33 suggest between position variations for Al, Ba, Ca, K, Mg, Mn, Na and P. More specific indications of spatial variability of elemental concentrations can be deduced from plots in Figures 12A, 12B, 13A, 13B and 14 and results of statistical analyses in Table 33. As for the soil figures, individual sampling concentrations in corn leaves, corn stalk and alfalfa are plotted for Al, Ba, Ca, Cu and Fe in Figures 12A and 12B, K, Mg, Mn, Na and P in Figures 13A and 13B, and S, Si, Sr, Ti and Zn in Figure 14. Typical analytical precisions are indicated by error bars on first or second points in each plot, and means  $\pm$  one standard deviation over all 10 sampling locations are included at the right of each figure compartment. Visual inspection of these plots can give the following indications: (a) variations of concentrations along the transect based on scatter of individual points (b) comparison of mean levels among the three tissues and (c) trends with location.

Spatial variability among sampling locations and concentration trends along the transects are summarized in Table 34. As previously, to establish significance of variation, visual t tests were made among all points in the plots. Significant variations were estimated to be present for Al, Mg, Mn, Na, P and Zn in generally both corn leaves and corn stalk and for Al, Ca, Mg, Na, P and Sr in alfalfa. Trends of increasing or decreasing concentration or the occurrence of one or more maxima/minima were observed for Al, Ca, Mg, Mn, Na, P, Sr, Ti and Zn in at least one crop.

Comprehensive statistical tests were carried out on concentration data for each element and all possible combinations of tissues. Results of these comparisons are summarized in Tables 35-37. Table 35 presents a concentration comparison, by element, for each of the three crop tissues, listing concentrations in sequence from highest to lowest and including comparison symbols. All t tests were carried out at  $p = 0.05$  and  $0.01$ ; all indicated differences are at  $p = 0.05$  with a number at  $p = 0.01$  also indicated in the Table. Many significant differences are exhibited. Out of a total of 45 statistical comparisons, 28 exhibited significant differences and 17 were identical. Some of the dominant overall comparisons gleaned from the Table are: corn leaf > corn stalk, corn leaf > alfalfa, corn stalk < alfalfa, corn leaf = corn stalk, corn leaf = alfalfa, and corn stalk = alfalfa. Summaries of element-specific comparisons are presented in Tables 36 and 37, covering in detail, the statistical behaviour of each element over all 45 possible comparisons for this population of data. It can be observed that of the 28/45 significant differences, the vast majority are highly significantly different indicating preferential uptake and deposition of major and trace elements in various crop tissues.



Table 32. Elemental concentrations (mg/kg) in corn crops from field 1<sup>1</sup>.

Element	Corn leaves			Corn stalks		
	Min.	Max.	Mean $\pm$ SD	Min.	Max.	Mean $\pm$ SD
Al	72	186	106 $\pm$ 32	42	102	63 $\pm$ 21
Ba	0	10	8 $\pm$ 4	10	10	10 $\pm$ 0
Ca	3590	5770	4590 $\pm$ 700	1780	3210	2570 $\pm$ 460
Cu	15.0	22.0	17.9 $\pm$ 2.5	3.0	8.0	5.3 $\pm$ 1.5
Fe	106	146	120 $\pm$ 11	46	81	63 $\pm$ 16
K	12700	21630	17630 $\pm$ 2990	11000	416000	26730 $\pm$ 9560
Mg	3230	6920	5070 $\pm$ 1610	3860	7910	5500 $\pm$ 1450
Mn	22	92	48 $\pm$ 22	21	69	33 $\pm$ 15
Na	13	55	24 $\pm$ 13	12	42	28 $\pm$ 12
P	2520	3040	2760 $\pm$ 190	1510	2600	2060 $\pm$ 310
S	1900	2280	2050 $\pm$ 140	820	1310	1030 $\pm$ 150
Si	159	348	266 $\pm$ 61	145	395	264 $\pm$ 75
Sr	16	28	21.8 $\pm$ 4.1	11	19	14.4 $\pm$ 2.8
Ti	4	12	7 $\pm$ 2	3	7	5 $\pm$ 2
Zn	16	46	35 $\pm$ 9	28	50	40 $\pm$ 6

<sup>1</sup> Based on analyses of 10 samples of each tissue taken from identical positions as the corresponding soil samples.

Table 33. Elemental concentrations (mg/kg) in alfalfa crops from field 2<sup>1</sup>.

Element	Min.	Max.	Mean $\pm$ SD
Al	40	131	69 $\pm$ 31
Ba	10	20	13 $\pm$ 4
Ca	15330	19350	17440 $\pm$ 1310
Cu	18	20	18.9 $\pm$ 0.8
Fe	68	104	80 $\pm$ 14
K	14480	20900	17640 $\pm$ 2090
Mg	4010	5750	4620 $\pm$ 620
Mn	12	21	16 $\pm$ 3
Na	58	479	177 $\pm$ 126
P	1681	2178	1950 $\pm$ 180
S	2478	3068	2840 $\pm$ 190
Si	92	165	118 $\pm$ 23
Sr	62	89	74.3 $\pm$ 9.5
Ti	3	7	4.2 $\pm$ 1.5
Zn	21	34	29 $\pm$ 5

<sup>1</sup> Based on analyses of 9 whole above-ground samples taken from identical positions as the corresponding soil samples.

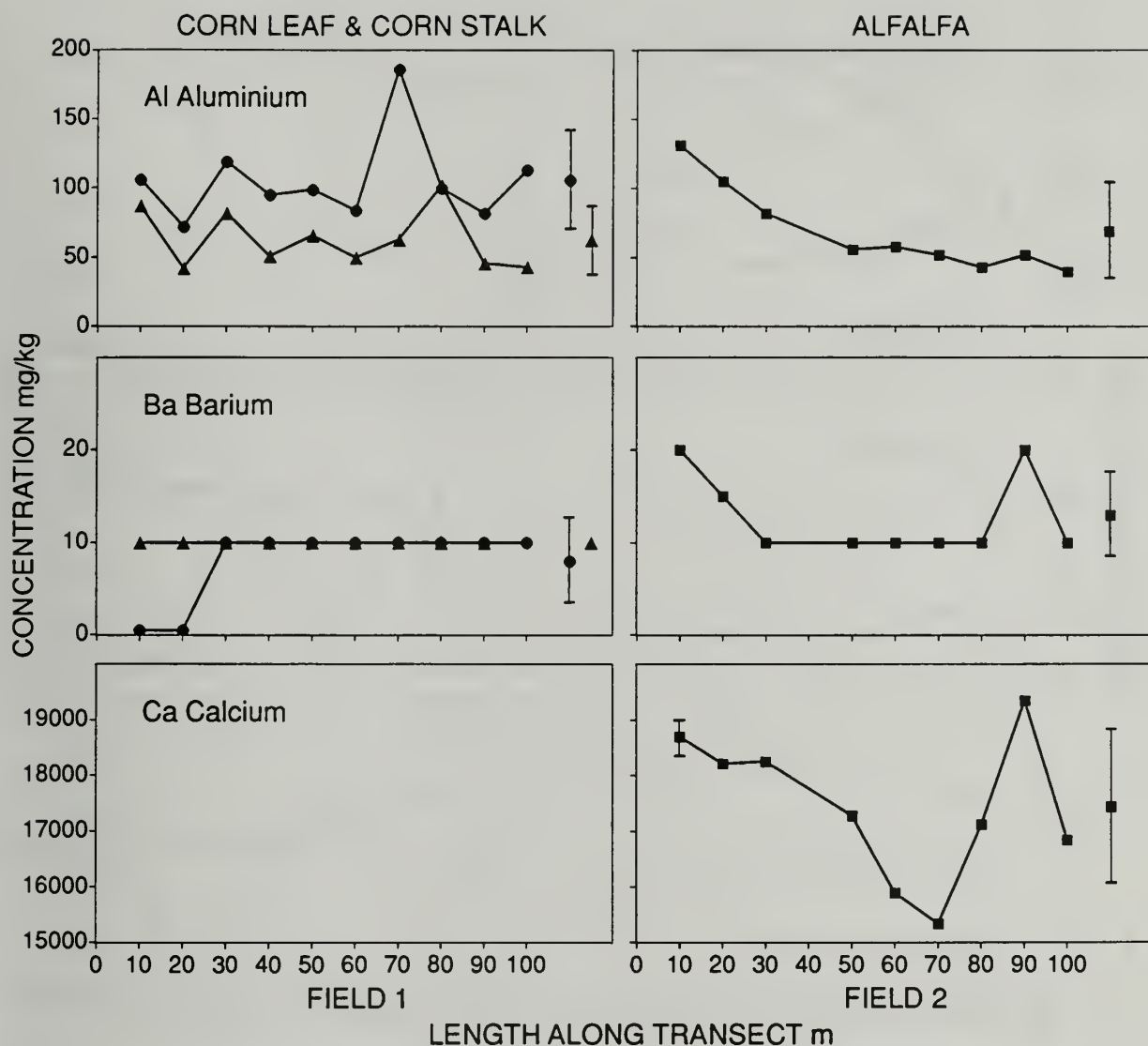


FIGURE 12A. Concentrations (mg/kg) of Al, Ba and Ca in crops from the two fields (•: corn leaf; ▲: corn stalk; ■: alfalfa; fields 1 and 2 seeded to corn and alfalfa, respectively). Typical one standard deviations of individual determinations (analytical precision) are indicated by error bars on first or second points of each plot. The absence of an error bar indicates that the uncertainty is within the dimensions of the point. The points at the right of each compartment (• ▲ ■) are means  $\pm$  one standard deviation (a measure of mean and variation with location) for the respective crops and tissues.

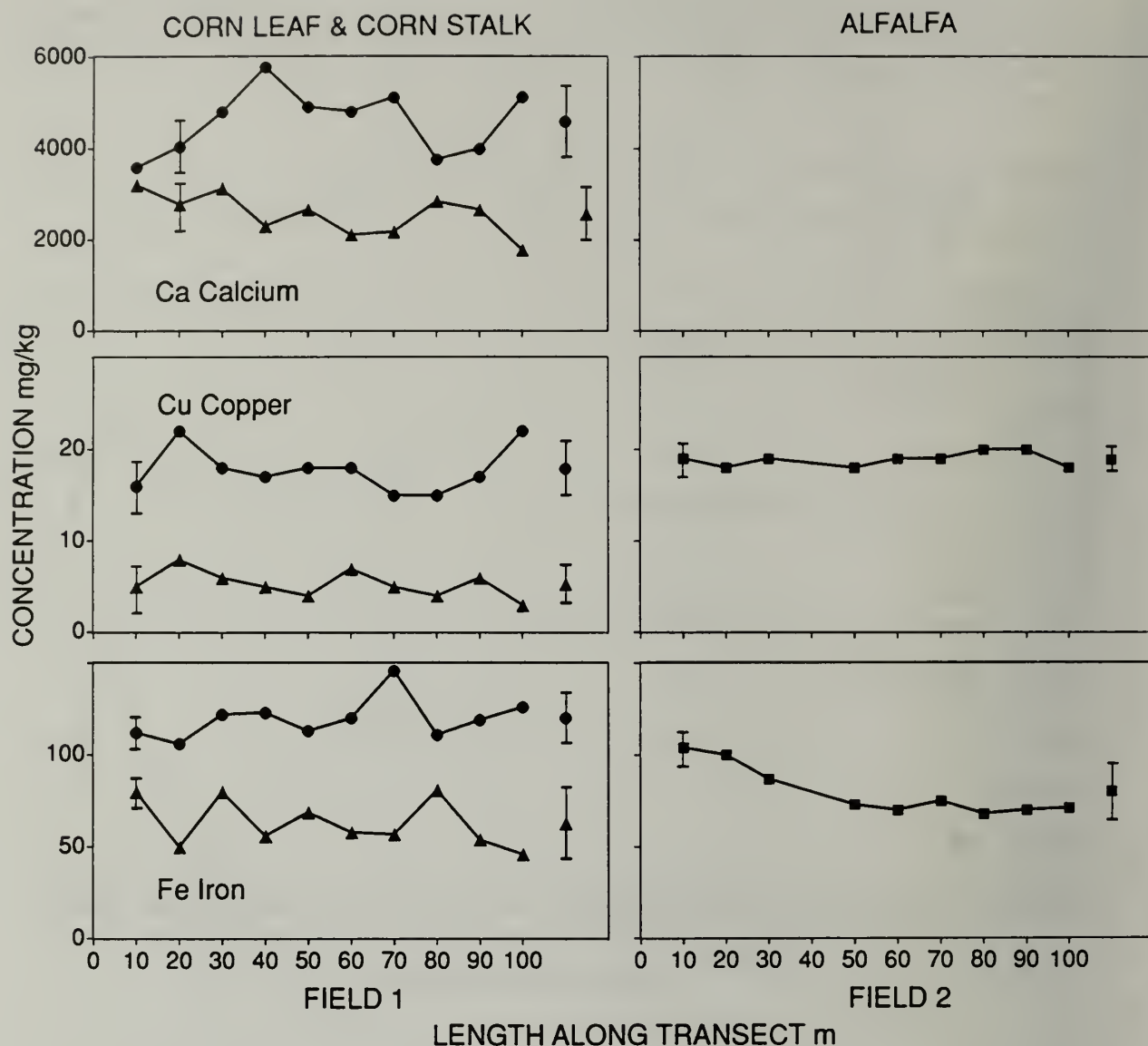


FIGURE 12B. Concentrations (mg/kg) of Ca, Cu and Fe in crops from the two fields (•: corn leaf; ▲: corn stalk; ◻: alfalfa; fields 1 and 2 seeded to corn and alfalfa, respectively). Typical one standard deviations of individual determinations (analytical precision) are indicated by error bars on first or second points of each plot. The absence of an error bar indicates that the uncertainty is within the dimensions of the point. The points at the right of each compartment (• ▲ ◻) are means  $\pm$  one standard deviation (a measure of mean and variation with location) for the respective crops and tissues.

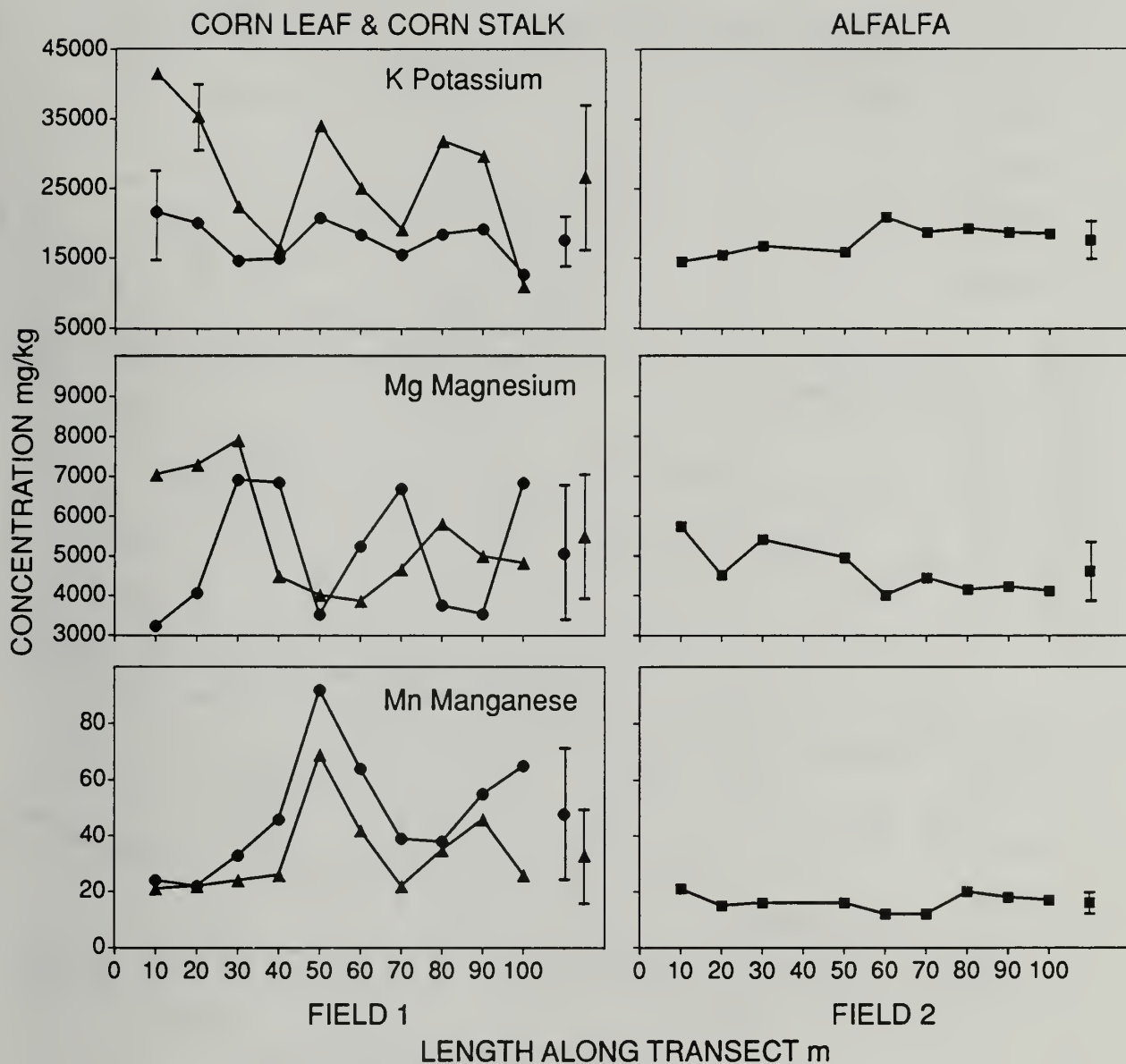


FIGURE 13A. Concentrations (mg/kg) of K, Mg and Mn in crops from the two fields (•: corn leaf; ▲: corn stalk; ■: alfalfa; fields 1 and 2 seeded to corn and alfalfa, respectively). Typical one standard deviations of individual determinations (analytical precision) are indicated by error bars on first or second points of each plot. The absence of an error bar indicates that the uncertainty is within the dimensions of the point. The points at the right of each compartment (• ▲ •) are means  $\pm$  one standard deviation (a measure of mean and variation with location) for the respective crops and tissues.



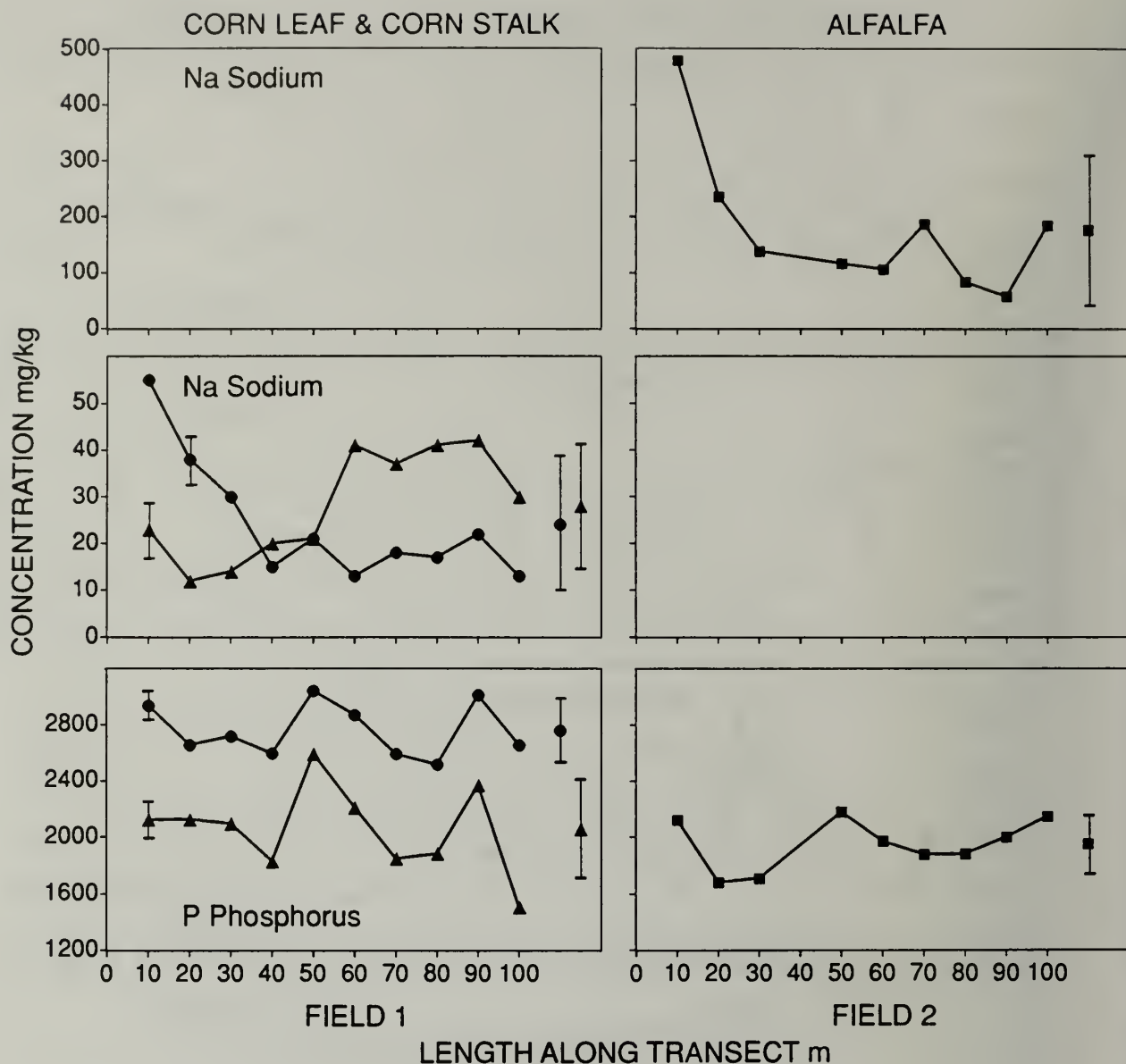


FIGURE 13B. Concentrations (mg/kg) of Na and P in crops from the two fields (•: corn leaf; ▲: corn stalk; ■: alfalfa; fields 1 and 2 seeded to corn and alfalfa, respectively). Typical one standard deviations of individual determinations (analytical precision) are indicated by error bars on first or second points of each plot. The absence of an error bar indicates that the uncertainty is within the dimensions of the point. The points at the right of each compartment (• ▲ ■) are means  $\pm$  one standard deviation (a measure of mean and variation with location) for the respective crops and tissues.

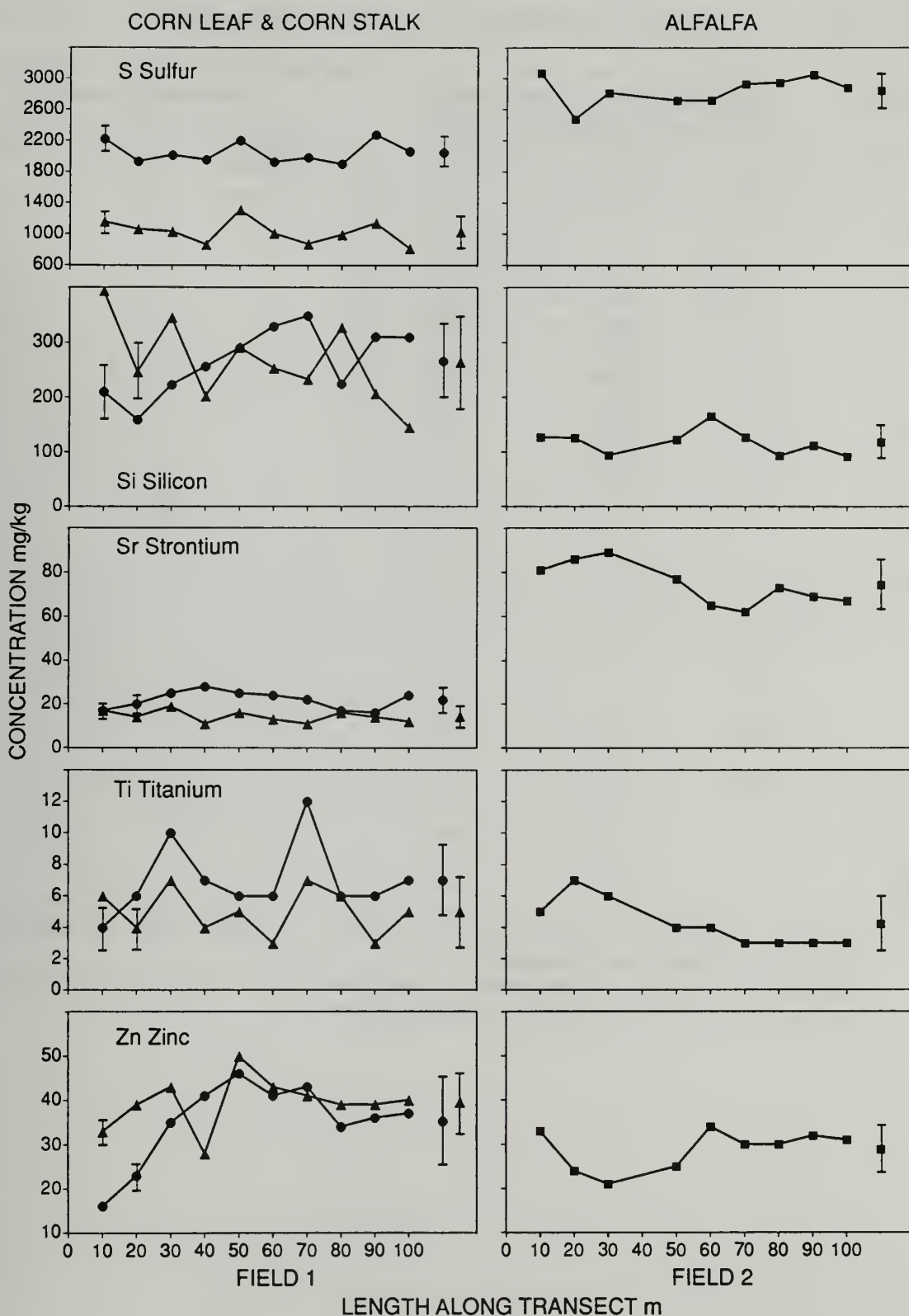


FIGURE 14. Concentrations (mg/kg) of S, Si, Sr, Ti and Zn in crops from the two fields (•: corn leaf; ▲: corn stalk; ■: alfalfa; fields 1 and 2 seeded to corn and alfalfa, respectively). Refer to caption to Fig. 6A for details.

Table 34. Variability of Elemental Contents in Crops

Element	Significant variation among position for <sup>1</sup>			Trend with position <sup>2</sup>		
	Corn leaves	Corn stalk	Alfalfa	Corn leaves	Corn stalk	Alfalfa
Al	S	S	S	N	N	↓
Ca	NS	NS	S	N	↓	M
Cu	NS	NS	NS	N	N	N
Fe	NS	NS	NS	N	N	N
K	NS	NS	NS	N	N	N
Mg	S	S	S	M	M	↓
Mn	S	S	NS	M	M	N
Na	S	S	S	↓	↑	↓
P	NS	S	S	N	M	N
S	NS	NS	NS	N	N	N
Si	NS	NS	NS	N	N	N
Sr	NS	NS	S	N	N	↓
Ti	NS	NS	NS	N	N	↓
Zn	S	S	NS	↑	N	N

<sup>1</sup> Based on visual t tests on figures 12A, 12B, 13A, 13B, 14 among the 10 positions along the transects.

<sup>2</sup> General trend of concentration along transect; ↑: increase; ↓: decrease; N: no trend; M: one or more maximum/minimum.

Table 35. Comparisons of Element Concentrations in Corn and Alfalfa Tissues<sup>1</sup>

Element	Concentration Comparison <sup>2</sup> (Highest to Lowest Sequence)
Al	Corn Leaf* > Alfalfa = Corn Stalk*
Ba	Alfalfa = Corn Stalk = Corn Leaf
Ca	Alfalfa > Corn Leaf* > Corn Stalk*
Cu	Alfalfa* = Corn Leaf* > Corn Stalk*
Fe	Corn Leaf* > Alfalfa > Corn Stalk*
K	Corn Stalk > Corn Leaf = Alfalfa
Mg	Corn Stalk = Corn Leaf = Alfalfa
Mn	Corn Leaf* = Corn Stalk* > Alfalfa*
Na	Alfalfa* > Corn Stalk* = Corn Leaf*
P	Corn Leaf* > Corn Stalk* = Alfalfa*
S	Alfalfa* > Corn Leaf* > Corn Stalk*
Si	Corn Leaf* = Corn Stalk* > Alfalfa*
Sr	Alfalfa* > Corn Leaf* > Corn Stalk*
Ti <sup>3</sup>	Corn Leaf* = Corn Stalk = Alfalfa*
Zn <sup>4</sup>	Corn Stalk* = Corn Leaf = Alfalfa*

<sup>1</sup> Based on t tests ( $p = 0.05$ ), with typically 18 degrees of freedom, of pairs of concentration means for corn in field 1 and alfalfa in field 2.

<sup>2</sup> Pairs of tissues both members of which are marked with an asterisk are significantly different at  $p = 0.01$ .

<sup>3</sup> Also Corn Leaf > Alfalfa at  $p = 0.01$ .

<sup>4</sup> Also Corn Stalk > Alfalfa at  $p = 0.01$ .

Table 36. Summary of Comparisons of Element Concentrations in Two Tissue Components of Corn in Field 1<sup>1</sup>.

Corn Leaf = Corn Stalk	Corn Leaf < Corn Stalk	Corn Leaf > Corn Stalk
Ba, Mg, Mn Na, Si, Ti Zn	K	Al*, Ca*, Cu* Fe*, P*, S* Sr*

<sup>1</sup> Based on t tests ( $p = 0.05$  and  $p = 0.01^*$ ) with 18 degrees of freedom. Elements with an asterisk exhibit significantly different concentrations at  $p = 0.01$ .

Table 37. Comparisons of Element Concentrations in Corn and Alfalfa Tissues<sup>1</sup>.

Corn Leaf = Alfalfa	Corn Leaf < Alfalfa	Corn Leaf > Alfalfa
Cu, K, Mg Zn	Ba, Ca*, Na* S*, Sr*	Al*, Fe*, Mn* P*, Si*, Ti*
Corn Stalk = Alfalfa	Corn Stalk < Alfalfa	Corn Stalk > Alfalfa
Al, Ba, Mg P, Ti	Ca*, Cu*, Fe Na*, S*, Sr*	K, Mn*, Si* Zn*

<sup>1</sup> Based on t tests ( $p = 0.05$  and  $p = 0.01$ ) with typically 18 degrees of freedom. Elements with an asterisk exhibit highly significantly different ( $p = 0.01$ ) concentrations.



### Correlations of Total Element Concentrations

In addition to correlations, reported previously, among extractable and total concentrations within given elements, extensive sets of correlation calculations were carried out among different elements. These correlations were established with respect to total concentrations of the 22 elements determined in soils plus an additional parameter, pH. Three sets of correlations were established: within surface Ap horizons of soils from the two fields, within subsurface Bg horizons of soils from the two fields (both for different pairs of elements) and between the two horizons (for identical or different elements); these are summarized in detail in Tables 38-40, respectively. Perusal of these tabulations leads to several interesting conclusions. The vast majority of correlations within either Ap or Bg horizons (Tables 38, 39) are positive; that is an increasing concentration of one element is matched by an increasing concentration of the second element of the pair in the correlation calculation. The vast majority of correlations between horizons (Table 39) are negative; that is an increased concentration of a given element in one horizon is matched by a decreased concentration of the same element in the other horizon. Also, in many of the cases where a significant correlation was evident at  $p = 0.05$ , it was also highly significant at  $p = 0.01$ , thus we have many highly significant correlations.

Although the number of correlations for fields 1 and 2 are similar for correlations within Ap and between Ap-Bg horizons (50% more correlations within Bg for field 1), these correlations are not necessarily for the same elements. Thus the two fields exhibit correlation differences and an attempt has been made to summarize this in Tables 41 and 42. In these tables, element pairs are listed for which highly significant correlations are evident in one field but no correlation in the other. In other words, one field has a  $p = 0.01$  (\* \*) correlation, the other has none for the listed pair of elements. A wealth of information is thus available for further assessment and interpretation regarding the elemental content of these two fields and possible effects of cultivation thereon.

Table 38. Correlations of Total Element Concentrations Within Surface (Ap) Horizons of Soils from Fields 1 and 2'.

	Al		Ba		Be		C		Ca		Co		Cr		Cu		Fe		K		La		Mg	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Al																								
Ba					*				-**				*	*			**	*	*	*	*			
Be													*	*	**	*					**	*	*	*
C																								
Ca													-*	*										
Co													*	*	*						**	*	*	*
Cr															*	*	**	**	*	*	*	*	*	*
Cu																**	**	**	*	*	*	*	*	*
Fe																								
K																								
La																								*
Mg																								
Mn																								
Na																								
Ni																								
P																								
Si																								
Sr																								
Ti																								
V																								
Yb																								
Zn																								
pH																								

1 Significant correlations at  $p = 0.05$  (\*) and  $p = 0.01$  (\*\*); negative correlations are indicated by -.

Table 38. (cont'd)

	Mn		Na		Ni		P		Si		Sr		Ti		V		Yb		Zn		pH	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Al			-*		**		*		-**		-**		*	**	*				**			
Ba	*					*																
Be			-*						-**				*		**	*						
C -**				-*			**															
Ca		**	**					**														
Co			-**	-**		**			-**	-**	-*	-*	**	**	**	**			**	**	**	*
Cr			-*		**				-**	-**			**	**	**	**			**	*		
Cu			-*		**	*			-**	-**			*	**	**	**			**	*		
Fe			-*	-*	**	**			-**	-*				**	**	**			**	*		
K												**					-**					
La	*								-*						**	**	*					
Mg	*		-*		**	**			-**	-*			*	*	**	**			**	*		
Mn															**	**						
Na									**	**	**	**	-*	-*	-*	-*			-*	-*	**	**
Ni					-*				**	**	**	**			**	**			*	*	**	**
P									-**	-**					**	**						
Si											**	*			-**	-**			-**	-**	-*	-*
Sr											**				-**	-**			-*	-*		
Ti													-*	-*	*							
V																			**	**		
Yb																						
Zn																			**	**		-*
pH																						

Table 39. Correlations of Total Element Concentrations Within Subsurface (Bg) Horizons of Soils from Fields 1 and 2<sup>1</sup>.

	Al		Ba		Be		C		Ca		Co		Cr		Cu		Fe		K		La		Mg	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Al																								
Ba																								
Be																								
C																								
Ca																								
Co																								
Cr																								
Cu																								
Fe																								
K																								
La																								
Mg																								
Mn																								
Na																								
Ni																								
P																								
Si																								
Sr																								
Ti																								
V																								
Yb																								
Zn																								
pH																								

<sup>1</sup> Significant correlations at  $p = 0.05$  (\*) and  $p = 0.01$  (\*\*); negative correlations are indicated by - .

Table 39. (cont'd)

	Mn		Na		Ni		P		Si		Sr		Ti		V		Yb		Zn		pH	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Al	*				*						-*		**	*			-*		*			
Ba					**	**			-*		-*										-*	
Be																						
C			-**						-*		-*						-**					
Ca		**	**					**	**	*	*				*		**					
Co	*		-*		*		-*		-*		-*				-**		-*					
Cr						-**																
Cu					**				-*		-**		**		-*				**			-*
Fe								-*	-*		-*				-*			**	**			
K	-*				*			-*	-*		-*				-*		-*	*	*			
La														*					*			
Mg					**				-*													
Mn																						
Na								**	**		**				*		**					
Ni								*	*	-*	*						*		*			
P																						
Si									*		*						*		*			
Sr								*	*		*				*		*		*			
Ti															*		*		-*			
V																						
Yb																						
Zn																			-*		-*	
pH																						



Table 40. Correlations of Total Element Concentrations Between Surface (Ap) and Subsoil (Bg) Horizons of Soils from Fields 1 and 2<sup>1</sup>.

	Al		Ba		Be		C		Ca		Co		Cr		Cu		Fe		K		La		Mg	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Ap																								
Bg																								
Al																								
Ba																								
Be																								
C								*												**				
Ca																								
Co								*																
Cr																								
Cu									-*				*											
Fe																								
K																								
La																								
Mg																								
Mn																								
Na																								
Ni																								
P																								
Si																								
Sr																								
Ti																								
V																								
Yb																								
Zn																								
pH																								

<sup>1</sup> Significant correlations at  $p = 0.05$  (\*) and  $p = 0.01$  (\*\*); negative correlations are indicated by - .

Table 40. (cont'd)

	Mn		Na		Ni		P		Si		Sr		Ti		V		Yb		Zn		pH	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Al									*						-*	-*						
Ba					-*																	
Be													-*									
C																	*		-*			
Ca			*				-**															
Co																						
Cr																						
Cu		-*							-**						-*	-*						
Fe															-*	-*						
K						*												*				-**
La																						
Mg			*																			
Mn							-*	-**									*					
Na																						
Ni																						
P																					-*	-*
Si																	*					
Sr			**		-*	-**			*	*					-*	-**			-**			-*
Ti									*	*												
V		-*																				
Yb															-*		-*					*
Zn									*													
pH																						

Table 41. Highly significant total element correlations specific to only one field<sup>1</sup>.

Correlations within Ap		Correlations within Bg	
only in T <sub>1</sub>	only in T <sub>2</sub>	only in T <sub>1</sub>	only in T <sub>2</sub>
Al - Ca (-)	Al - Fe	Ca - Si	Be - Cu
Al - Ni	C - P	Cr - P (-)	C - Na (-)
Al - Si (-)	Co - La	Na - Si	C - Yb (-)
Al - Sr (-)	Co - Ni	Si - Sr	Cr - Yb (-)
Al - Zn	Co - V		Cu - Ni
Be - Si (-)	Cr - Ti		Fe - Ti
C - Mn (-)	Fe - Ni		K - Mg
Ca - Na	Ni - pH		Mg - Ni
Ca - Sr	Ni - Si		
Cu - Si (-)			
K - Ti			
K - Yb (-)			
Mn - pH			
Na - Sr			

<sup>1</sup> Highly significant (p = 0.01, indicated as \*\* in previous tables) correlations observed as indicated and absent (no correlation) in the other field. Negative correlations are indicated by negative signs in parentheses.

Table 42. Highly significant total element correlations between the soil horizons Ap and Bg specific to only one field<sup>1</sup>.

Correlations only in Field 1	Field 2
Fe (Bg) - Be (Ap) (-)	Ba (Bg) - Co (Ap) (-)
Ti (Bg) - Zn (Ap) (-)	C (Bg) - K (Ap)
pH (Bg) - Co (Ap)	Ca (Bg) - P (Ap) (-)
Na (Bg) - C (Ap) (-)	Cu (Bg) - Sr (Ap) (-)
	K (Bg) - Cu (Ap) (-)
	La (Bg) - pH (Ap) (-)
	Ti (Bg) - Co (Ap) (-)
	Ti (Bg) - Na (Ap)
	Zn (Bg) - Be (Ap) (-)

<sup>1</sup> Highly significant (p = 0.01, indicated as \*\* in previous tables) correlations observed as indicated and absent (no correlation) in the other field. Negative correlations are indicated by negative signs in parentheses.

## Role of Soil Amendments

An idea of what role the fertilizer may play in contributing elements to the soil can be surmised by considering the elemental content of the fertilizer and its rate of application. Table 43 lists median concentrations of a number of trace elements in N, P, K, and organic (including manure) fertilizers estimated from the comprehensive compilations published by Swaine (1962) covering an extensive range of fertilizers and sources throughout the world. Median trace element contents for elements of interest in this work, range from 0 mg/kg for Be, Ti and V in some classes of materials to 600 mg/kg for Sr in P fertilizers. Based on these median estimates, and estimates of dry weight additions (kg/ha/yr) of the following amounts of fertilizers: 500 kg (N fertilizer), 300 kg (P fertilizer), 150 kg (K fertilizer) to field 1 corresponding to the 120 - 30 - 70 kg/ha N-P-K mentioned earlier, and 10,000 kg (manure) to field 2, annual contributions of trace elements to the soil plow layer are listed in columns 6-9 of Table 43. These estimates of annual contribution were calculated taking the weight of the plow layer to be  $2 \times 10^6$  kg/ha and assuming uniform mixing. Trace element contributions range from 0 mg/kg for several elements to ca 0.1 mg/kg for Mn, Sr, Ti and V from N, P, K fertilizers, and close to 1 mg/kg for Mn, Sr and Zn from organic fertilizers.

These contributions are cast in another perspective in Table 44 where they are related to mean total and extractable (DTPA only, for purposes of discussion) trace element concentrations in the studied soils; two major nutrients, K and P are also included. Contributions, expressed as a percent of the total elemental content of the soil, range up to ca 1% for Zn and 2% for P, typically less than 1%. Expressed as a percent of the extractable content, percent contributions are substantially higher, up to 70% for Zn. This data is along the findings of others researchers (Frank et al., 1976) that fertilizers do not necessarily contribute overwhelming quantities of trace elements compared to the total elemental content of the soil. Keeping in mind, however, that median trace element fertilizer content values were used in these calculations, significantly more trace element may be added from trace element rich fertilizers containing higher than median amounts. Also, the additions will be tempered by removal by the crop, not considered here, but augmented by long term usage of the fertilizer. Contributions, in relation to extractable levels, are substantially greater. Thus, fertilizer contributions of trace elements cannot be ignored in explaining differences observed between the two fields, a topic worthy of follow up consideration.

Table 43. Minor Elemental Content of Fertilizer and contribution to Soil plow layer (mg/kg).

Element	Median concentration in				Annual Contribution to soil plow			
	N	P	K	Organic	N	P	K <sub>2</sub>	Organic
	Fertilizer				layer from Fertilizer			
Ba	40	75	0.1	50	0.01	0.01	0	0.25
Be	0 in various fertilizers				0 from various fertilizers			
Co	0	2	0.01	0.7	0	0	0	0.004
Cr	0	220	10	6	0	0.033	0.001	0.03
Cu	2	25	5	22	0.001	0.004	0	0.11
La	10 in various fertilizers				0.003 from various fertilizers			
Mn	5	575	6	135	0.001	0.09	0	0.7
Ni	0.1	8	0.5	3.5	0	0.001	0	0.02
Sr	25	600	33	144	0.006	0.09	0.002	0.7
Ti	0	500	0	40	0	0.08	0	0.2
V	0	400	0	0.5	0.06	0	0.003	
Yb	9 in various fertilizers				0.002 from various fertilizers			
Zn	5	150	1.2	120	0.001	0.02	0	0.6

<sup>1</sup> Medians on a dry basis etimated from extensive compilations by Swaine (1962).

<sup>2</sup> Based on median contents and dry weight additions (kg/ha/annum) of the following amounts of fertilizer: 500 kg (N fertilizer); 300 kg (P fertilizer); 150 kg (K fertilizer); 10,000 kg (organic fertilizer - manure) and weight of soil plow layer taken as  $2 \times 10^6$  kg/ha.



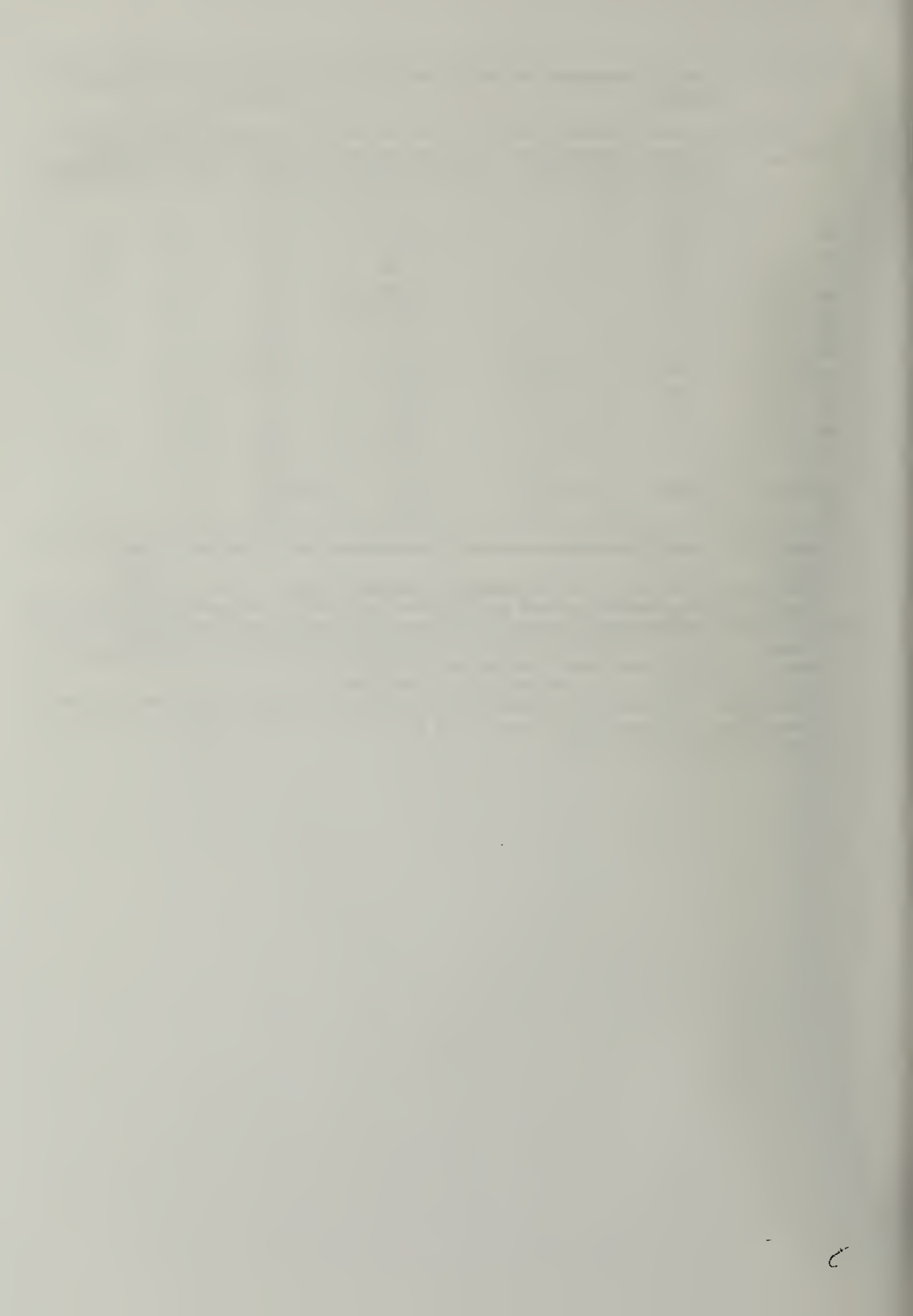
Table 44. Annual Contributions of Elements by Fertilizer to Soil plow layer (mg/kg).

Element	Concentration in soil <sup>1</sup>		Concentration added by <sup>2</sup>		Percent of <sup>3</sup>	
	Total	Extractable	NPK Fertilizer	Manure	Total	Extractable
Ba	970	0	0.02	0.3	0.03	-
Co	15	0.2	0	0	0	0
Cr	80	0.2	0.03	0.1	0.1	50
Cu	21	1.4	0.01	0.1	0.5	7
La	30	-	0.003	-	0.01	-
Mn	560	17	0.1	0.7	0.1	4
Ni	36	0.5	0.001	0.02	0.1	4
Sr	340	-	0.1	0.7	0.2	-
Ti	4080	-	0.1	0.2	0.005	-
V	81	-	0.1	0	0.1	-
Yb	2	-	0.002	-	0.1	-
Zn	71	0.9	0.02	0.6	0.8	70
K	21320	-	35	100	0.5	-
P	900	-	15	30	3	-

<sup>1</sup> Mean total and DTPA-extractable concentrations in Ap horizon found in this work.

<sup>2</sup> Estimates of concentrations added by summing contributions from NPK fertilizers and taking values for organic fertilizers equal to those in manure applied to these fields. Values for K and P in manure are based on estimated concentrations of 20,000 mg K/kg and 6,000 mg P/kg (Richars and Mantel, 1991). Note that these are annual estimated contributions and do not consider impact of many years of continued fertilizer addition.

<sup>3</sup> Elemental contribution by fertilizer, using the higher of values for NPK fertilizer or manure, expressed as a percentage of the total or extractable concentration in the soil.



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